PHYSICO-CHEMICAL METHODS

FOREWORD TO SECOND VOLUME

THE first volume dealt in the main with types of measurement and with essential apparatus. In the present volume we are more concerned with practical applications: separation processes, optical and electrical measurements, including Hydrogen-ion and Dielectrics. A chapter on Colloids is included; the brevity of the treatment is to be explained by the existence of numerous special treatises on this subject.

Dr. P. Cohen Henriquez, has completely revised the chapter on Dielectrics and has extended it to include recent work in this important branch of physical chemistry. The chapter on Thermionic Vacuum Tubes has been revised and rewritten by Mr. G. W. Warren, B.Sc., of the Research Staff of the General Electric Company. Dr. C. O. Ceallaigh of University College, Cork, has written the new chapter on Radioactivity. Mr. Desmond Reilly has helped with the proofs.

It is hoped that the treatment here provided, will be found to be of practical use in the training of a physical chemist and will serve as a general conspectus of the subject in the case of more specialized workers. The 'Suggestions for Further Reading', which are continued in the present volume, are intended to increase the usefulness of the work as an introduction to the more detailed investigation of special topics.

Any attempt to deal in adequate detail with all the branches now included in physical chemistry would require the publication of a many-volumed encyclopædia written by a team of specialists. We feel, however, especially in view of the welcome accorded to the two previous editions, that there is room for a more modestly conceived general introduction. Nevertheless, as certain topics are of increasing importance, we have in mind the later publication of a supplementary volume. We refer in particular to an extended up-to-date treatment of gas manipulation, micro-methods (especially in biochemistry), solvent extraction, electrochemistry, photo-physical and photo-chemical processes.

We shall be grateful for a continuation of the co-operation of readers and of colleagues; suggestions, criticisms and information will be welcomed by the authors.

December 1939 ..

J. R.

W. N. R.

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VOLUME II

PRACTICAL MEASUREMENTS

CHAPTER I *

GASES AND VAPOURS

SECTION I: VAPOUR PRESSURE MEASUREMENTS

FOR any given temperature, below the critical temperature, there is a definite pressure at which a liquid and its saturated vapour are in equilibrium. This pressure is the vapour pressure of the liquid for that temperature. When liquid is introduced into the Torricellian vacuum over a barometer, it evaporates until the mercury has fallen an amount equal to the vapour pressure of the liquid, when evaporation ceases. This furnishes a direct measure of the vapour pressure; methods of this type, i.e. direct pressure measurements, are known as *static* methods. Other more indirect methods are usually of the *dynamic* type.

The vapour pressure of a liquid (or a solid) increases with rise of temperature, and the rate of increase is given by the Clausius-Clapeyron equation which may be written:

$$\frac{dp}{dT} = \frac{JL}{(v - v')T} \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

where dp/dT is the rate of change of vapour pressure with temperature, i.e. the slope of the vapour pressure curve,

     L is the latent heat of vaporization of a gram molecule
     v the volume of a gram molecule of the vapour
     v' that of the other phase (solid or liquid) and
     T the absolute temperature
     J = the mechanical equivalent of heat

Neglecting v', which is small in comparison with v, and replacing v by RT/p, the equation becomes

$$\frac{dp}{dT} = \frac{L}{R'T^2} \cdot p \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

$$\text{(where } R' = R/J = 1 \cdot 985 \,^{[1]})$$

on integration this gives

$$\ln p = \frac{-L}{R'T} + \text{constant} \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

or

$$\log_{10} p = \text{const.} - \frac{1}{T} \cdot \frac{L}{1 \cdot 985 \times 2 \cdot 303} \qquad . \qquad . \qquad (4)$$

and over a small temperature interval

$$\log_{10} p_1 - \log_{10} p_2 = \frac{L}{4 \cdot 571} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \qquad . \qquad . \qquad (5)$$

[1] See Vol. I, 105.

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A fuller study of the Clausius-Clapeyron equation is given on page 77 in connection with the value of the constant in equation (4), &c., and the relation of vapour pressure to that of Latent Heat. The Ramsay-Young and Dühring equations for vapour pressure-temperature relationships are also explained in the light of the above equations.

Example. The following values were found by Regnault for the vapour pressure of carbon disulphide :

Temperature	$-20°$	$-10°$		$+10°$	$+20°$
Vapour pressure in cm. of Hg .	4·73	7.94	12·8	19·8	29·8

converting the pressures to dynes per square centimetre and temperatures to the absolute scale we have :

p dynes per sq. cm.	$T°$ K	$\dfrac{1}{T}$	$\log_{10} p$	Calculated V.P. in cm. of Hg.
$6·32 \times 10^4$	253	$3·952 \times 10^{-3}$	4·8007	4·73
10·60	263	3·802	5·0253	7·93
17·10	273	3·663	5·2330	12·76
26·42	283	3·533	5·4219	19·86
39·77 .	293	3·413	5·5996	29·99

when $1/T$ is plotted against $\log p$ the values are found to lie on a straight line and extrapolating we find that when $1/T = 0$, $\log p = 10·673$, and this gives the constant in the equation which now becomes

$$\log p = 10·673 - \frac{1}{T} . \frac{L}{4·571} \qquad . \qquad . \qquad . \qquad (6)$$

substituting the first pair of values

$$4·801 = 10·673 - 3·952 \times 10^{-3} . \frac{L}{4·571}$$

and $L = 6789$ calories (molecular latent heat)

the molecular weight of carbon disulphide being 76, the latent heat of vaporization per gram is 89·3 calories.

Equation (6) now becomes[1]

$$\log p = 10·673 - \frac{1}{T} . 1486$$

The values of the vapour pressure given in the last column above were calculated from this equation and show satisfactory agreement with experiment. Another check on the equation is to calculate the boiling-point at atmospheric pressure, i.e. put p equal to $1·013 \times 10^6$ and calculate T : it will be found to be 45·4°, the actual value being 46·2°.

Static Measurements. The fundamental method indicated above does not need much description ; two barometer tubes must be used, standing side by side in the same trough ; the liquid is introduced in small quantities into one by means of a bent tube until the vapour above the

[1] *Cf.* Vol. I, p. 118.   Note $B = 4·6$, $T_b = 4·6 \times 319 = 1468$.

mercury is seen to condense on the glass wall; the fall in height of the mercury is then read by comparison with the second barometer. For accurate results, the liquid must be purified and freed from dissolved air before use. The barometer must be prepared carefully to ensure a perfect vacuum at the top; the usual method is to boil the mercury in the tube, the latter being nearly full and with the open end uppermost. The boiling should begin at the lower end so as to drive all air out with the vapour.

During a measurement the tube may be heated to the required temperature by enclosing it in a glass jacket through which vapour boiled from a convenient liquid is circulated. The same liquid may be used for a number of temperatures by varying the pressure in the jacket (Fig. 1 (I *)).
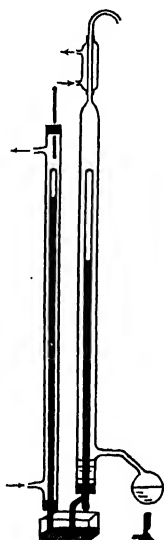
FIG. 1 (I *) FIG. 2 (1 *)
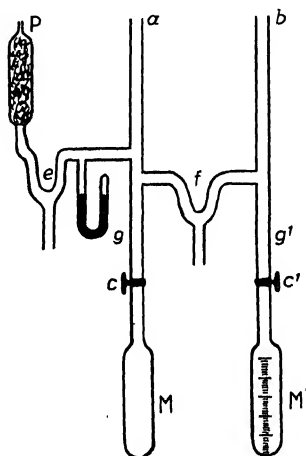
This method of measurement has not been generally employed for accurate work owing to many unavoidable practical objections. Static methods are now used more for comparative working than absolute measurement. The static method has been used by Frowein, Schkottky, and others for the measurement of the aqueous tension of hydrated salts. The barometer is replaced by a siphon manometer. Frowein's apparatus is shown in an earlier chapter, where it is employed for the comparison of vapour pressures. The dry hydrated salt is placed in the small flask f and concentrated sulphuric acid in f_1. The manometer limbs are filled with oil of negligible vapour pressure. Before sealing, the apparatus is evacuated by means of a pump. When equilibrium has been attained the depression in the oil column is read. The density of the oil being known, the reading can be standardized.

Differential manometers have been used for the determination of differences in pressure between solutions and pure solvents. Dieterici used a membrane with a pointer attached to register the pressure difference; Smits used a micro-manometer on the same principle as that described

as ' Roberts' Micro-manometer '. Tower used a mercury gauge designed by Morley. Tower's vapour-pressure apparatus is shown in Fig. 2 (I *). P is a drying tube containing phosphorus pentoxide on glass wool, and leads to a mercury pump ; g is a small manometer ; e and f are mercury valves ; M and M^1 are tubes of Jena glass, holding about 100 ml. for the liquids being compared ; a and b are connected to the delicate mercury gauge. The apparatus is evacuated through P and the bulbs placed for some time in a constant-temperature bath ; the pressure difference is then read with the delicate gauge.

A number of methods for the comparison of vapour pressures have been described elsewhere in this book and will not be further dealt with.

In general the static methods have not been found as convenient or as trustworthy as the dynamic ones. A method of the latter type should be used where possible for trustworthy working.
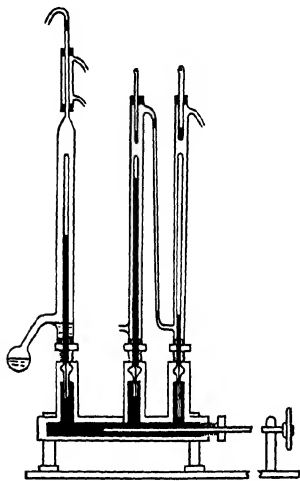
High Vapour Pressures. For the determination of vapour pressures at high temperatures a pressure apparatus similar to that used by Andrews in his research on carbon dioxide may be employed. Ramsay and Young have used this in their extensive high-temperature determinations. The apparatus is shown in Fig. 3 (I *). The lower unshaded portion is of iron or steel, the dark portion is enclosed mercury. The three vertical frames are topped by three glass tubes, two of which contain carbon dioxide, free air, and the third the liquid under experiment. The first two are used as air manometers, as described later. They are surrounded by jackets conveying water at constant temperature. The experimental tube is surrounded by a jacket carrying a boiling vapour as in the previous barometric method. The temperature of the vapour can be varied by increasing or lowering the pressure in the jacket. The manometer in the centre is for moderately high pressures. It is calibrated against a mercury-column gauge and then used to standardize the apparatus on the right.

The plunger in the base serves to diminish the internal volume of the apparatus and so compress the liquid vapour and the air in the manometers.

The usual corrections in reading the pressure must be made.

Dynamic Methods. The ' dynamic ' method was first used by Regnault in 1845. It is based upon the principle that when an inactive gas is saturated with the vapour the following relation holds :

$$\frac{\text{total volume}}{\text{volume of vapour}} = \frac{\text{total pressure}}{\text{pressure of vapour}}$$

The vapour pressure may therefore be calculated from a knowledge of the total volume, the total pressure, and the amount of vapour. The usual

method is to pass a known volume of air or other inert gas through or over the experimental substance at a known pressure and absorb and estimate the substance carried over. Walker at Ostwald's suggestion determined the ratio of the vapour pressures of solution and pure solvent by aspirating an air current first through the solution and then through pure water contained in Liebig potash bulbs, and absorbing the vapour in sulphuric acid. The loss of weight of the water is to the increase in weight of the acid as the difference in the vapour pressures is to that of pure water. The only essential in the experiment is to have the whole apparatus at the same temperature. Will and Bredig repeated the experiment with alcoholic solutions as already described. Perman applied the method directly to estimate the vapour pressures of water at different temperatures with reliable results. The bulbs were enclosed in a thermostat and absorption took place in sulphuric acid (Fig. 4 (I *)). An aspirator was used for the suction of the air and a manometer attached to the last bulb, which was
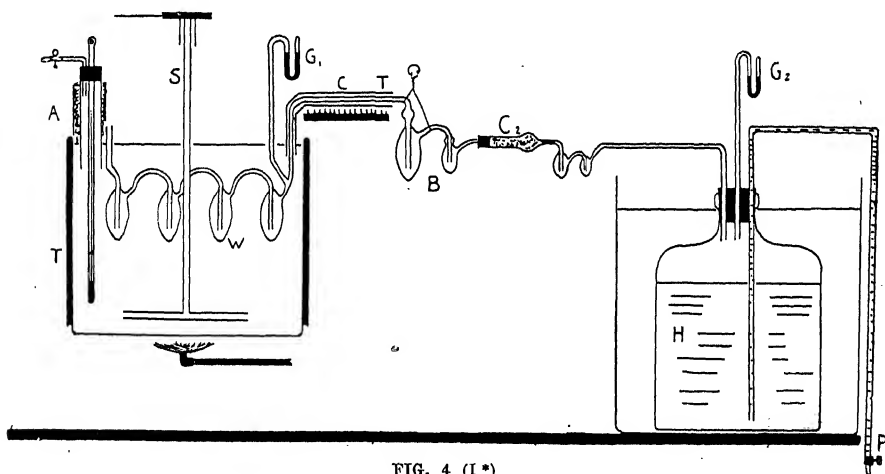
FIG. 4 (I *)

read by a mirror scale. The values for the vapour pressure obtained were found to agree very well with accepted values. Kahlenberg has described a somewhat similar method, as also have Berkeley and Hartley. The latter believe the bubbling method is subject to error through splashing, &c., and pass the air over the liquids instead of through them. Their principle is the same as that of Walker and Ostwald. Their assembled apparatus is shown in diagram (Fig. 5 (I *)). The air enters at A, where it is filtered through cotton-wool; it then passes into B, which is nearly filled with beads moistened with sulphuric acid. It is then led to the glass spiral C, where it takes up the temperature of the bath, and then into the sulphuric acid vessel D, where it is completely dried. From D it passes to the train of weighed vessels, E, F, G and H, into a 15-litre bottle I.

E and F contain the solution and G and H the water and sulphuric acid respectively. The bottle I damps any pressure changes caused by bubbling. The rate of passage of the air is seen by the rate of bubbling through J. The platform on which the vessels stand in the bath is made

to oscillate by means of a mechanical arrangement to cause a flow of the liquid in each vessel.

Von der Plaats passed a known volume of inert gas through pure mercury so as to saturate it with mercury vapour. The mercury was then collected by absorption and weighed. His values, however, are not accepted.
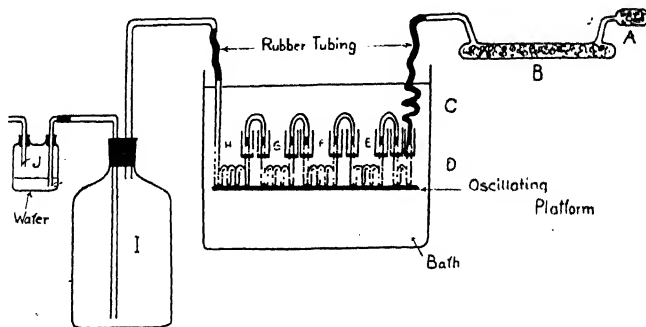
FIG. 5 (I *)

Morley describes a similar experiment, in which the loss of weight of the mercury was determined. The results obtained appear to be reliable. Briggs describes the measurement of the vapour pressures of concentrated sulphuric acid solutions by the air-bubbling method.

The air-current method has been used by Arctowski, who measured the rate with which powdered iodine volatilized in a current of dry air of constant velocity. Wiedermann, Stelzner, and Wiederschulte passed
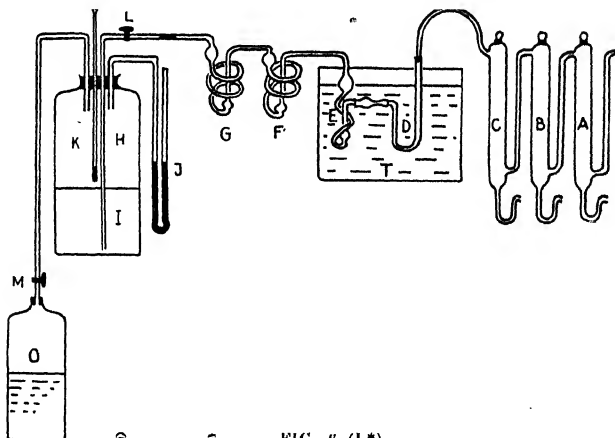
FIG. 6 (I *)

measured quantities of air over iodine in a tube and determined the loss in weight. Baxter, Hickey and Holmes have also determined the vapour pressure of iodine by this method. A measured volume of dry air was passed over pure iodine and then into a solution of sodium sulphite to absorb the volatilized iodine. From the sulphite solution the iodine was precipitated as silver iodide which was collected and weighed. Their

apparatus is shown in Fig. 6 (I *). A, B, and C are tubes of potassium hydroxide and sulphuric acid for drying and purifying the air. D contains the iodine and E the sulphite. F and G are auxiliary sulphite tubes. H is the aspirator bottle fitted with a mercury manometer and a thermometer. The volume of water run out of the aspirator was measured in vessel O.

Method of Ramsay and Young. Ramsay and Young have described a different dynamic method for the determination of vapour pressures. In Fig. 7 (I *), A is a vertical tube, closed at the top by an accurately fitting rubber stopper perforated with two holes, through one of which a thermometer passes. The bulb of the thermometer is covered wit͡ wool. Through the other hole is inserted a short narrow gla
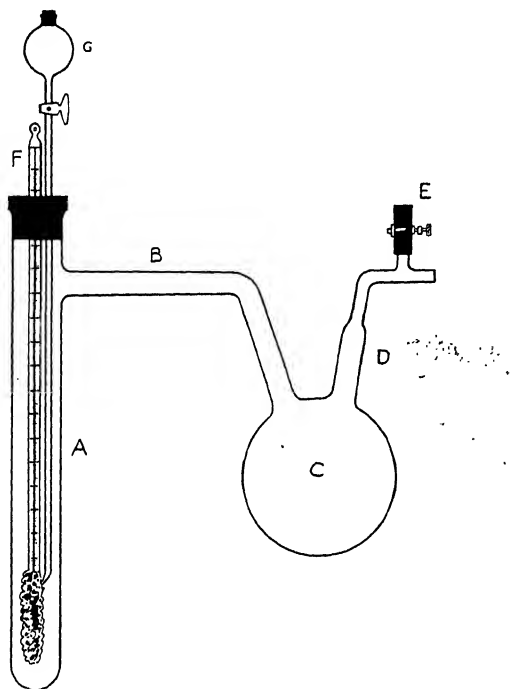
FIG. 7 (I *)   FIG. 8 (I⁴)
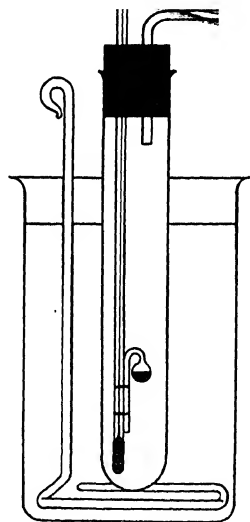
to a point at its lower end and slightly curved so that the point touches the thermometer. The other end of this tube carries a small reservoir and stopcock. At B a side-tube, 15 mm. in diameter, is sealed on. This leads to condenser C. The exit of this at D leads to a pump and manometer. A side-tube E, closed with a clip, serves to admit air when necessary.

The tube A may be heated by a water or paraffin bath or it may be jacketed with a wider tube and vapour passed round it. The condenser may be cooled in a freezing mixture if necessary.

The apparatus is exhausted, first by means of the pump. Liquid is allowed to enter from G and wet the cotton-wool round the thermometer. The tube is then heated, the temperature of the bath being kept 20° above that of the thermometer. When constant the temperature and pressure

are read. The pressure is then the vapour pressure of the liquid for this temperature. Air may then be admitted to raise the pressure and the reading repeated.

The method is found to give very reliable results. The cotton-wool allows perfectly free evaporation round the thermometer bulb and prevents superheating or other defects. The liquid is in contact with its vapour only as the air around the bulb will be displaced upwards first. The method was used by Reilly and McCarthy for solid vapour-pressure determinations of tribromophenol by coating the bulb with the solid and surrounding it with cotton-wool or asbestos.

For moderately accurate determinations of vapour pressure, the simple apparatus of Smith and Menzies described later under the heading of Boiling-points may be used. The construction of the apparatus is the same, but the thermometer and bulb are enclosed in a test-tube containing liquid before being placed in the open bath (Fig. 8 (I *). The L-tube leads to a manometer with connexions to the atmosphere and a pump. The pressure limits cannot be made extreme owing to the loose stopper on the test-tube. When the vapour pressure at a certain temperature is required, the apparatus is first brought to that temperature and kept constant for a little time. The stopcock connecting with the pump is then opened. When the pressure has fallen just below the vapour pressure, a continuous stream of bubbles issues from the capillary. A few moments suffice to displace the air in the capillary, and also any gases dissolved in the liquid. The connexion with the pump is then closed and air is very gradually admitted until the emission of bubbles suddenly ceases. The manometer is then read. When the vapour is soluble in the liquid the position of the meniscus in the capillary indicates the critical point.

To make sure that dissolved or adhering gases are all removed, the pressure is lowered and the boiling-out and subsequent operations repeated under a constant reading is obtained.

The hydrostatic pressure on the vapour in the bulb must be taken into account in estimating this pressure.

The following tables give the vapour pressures of water and potassium hydroxide solutions at temperatures generally experienced in the measurement of nitrogen from combustion analyses :

VAPOUR PRESSURE OF WATER

Temp.	Press. mm. Hg.	Temp.	Press. mm. Hg.	Temp.	Press. mm. Hg.	Temp	Press mm. Hg.
5	6·5	12	10·4	19	16·3	26	25·2
5·5	6·7	12·5	10·8	19·5	16·8	26·5	26·0
6	7·0	13	11·1	20	17·4	27	26·8
6·5	7·2	13·5	11·5	20·5	17·9	27·5	27·5
7	7·4	14	11·9	21	18·7	28	28·3
7·5	7·7	14·5	12·3	21·5	19·4	28·5	29·2
8	8·0	15	12·7	22	19·8	29	30·1
8·5	8·3	15·5	13·1	22·5	20·4	29·5	31·0
9	8·5	16	13·5	23	21·0	30	31·9
9·5	8·8	16·5	14·0	23·5	21·7	30·5	32·8
10	9·1	17	14·4	24	22·4	31	33·7
10·5	9·4	17·5	14·8	24·5	23·1	31·5	34·7
11	9·8	18	15·3	25	23·8	32	35·7
11·5	10·1	18·5	15·8	25·5	24·5	32·5	36·8

VAPOUR PRESSURE OF POTASSIUM HYDROXIDE SOLUTIONS

Temperature								40 grams potassium hydroxide + 100 ml. water	49 grams potassium hydroxide + 100 ml. water
10	.	.	.	.	.	.	.	6·5	5·6
12	.	.	.	.	.	.	.	7·5	6·5
14	.	.	.	.	.	.	.	8·5	7·4
16	.	.	.	.	.	.	.	9·6	8·3
18	.	.	.	.	.	.	.	10·9	9·5
20	.	.	.	.	.	.	.	12·4	10·8
22	.	.	.	.	.	.	.	13·9	12·1
24	.	.	.	.	.	.	.	15·5	13·4

Vapour-Pressure Hygrometer. Dowling [1] describes an apparatus which determines the moisture content of the air directly in terms of the aqueous vapour thereof. An air sample of fixed volume is exposed to a chemical drying agent and the reduction in pressure is observed. The apparatus, although not of the highest accuracy, is convenient.

A brass cylinder is furnished with a side chamber which contains the desiccating agent and has connected to it an oil manometer (U-tube). In the cylinder are two closely fitting pistons which are carried on a long rod so as to enclose an air space of fixed volume. The pistons are lubricated with a suitable oil to prevent air leakage. When the rod is pushed in, the first piston and one end of the second piston extend beyond the cylinder so that the ' air space ' is exposed to the open air. On slowly withdrawing the rod a sample of air is entrapped, and when the rod is fully out comes into communication with the drying chamber. Absorption of moisture is complete in 5 or 6 minutes and the resulting reduction of pressure is read off from the gauge. The vapour pressure in millimetres of mercury is given by

$$p = f.h$$

where h is the difference of pressure shown by the gauge and f is a factor depending on the ratio of the densities of the oil and mercury and on the ratio of the whole ' dead space ' to the volume of the air sample. The factor f is determined experimentally by placing a tubular cup lined with a strip of wet blotting-paper over the end of the brass tube so that on working the instrument a sample of air saturated with water vapour at the temperature of the room is drawn into the instrument. Then $f = p_{sat.}/h$ and the saturation vapour pressure can be obtained from the tables.

Humidity Tester. In this connexion may be mentioned the moisture tester made by the Cambridge Scientific Instrument Co. for measuring the moisture content of materials such as tea, grain, or any powdered or granular substance which is an electrical insulator in the dry state. The principle of measurement is based on the fact that the presence of absorbed moisture increases the Dielectric Constant of the material. A condenser made in the form of a container is packed with a known weight of the material under test and inserted in one arm of a condenser network ; its capacitance is then balanced by a calibrated condenser, the reading of the latter giving an indication of the moisture present. For accurate work it is first necessary to plot a curve showing the relation between the instru-

[1] *J. Sci. Inst.*, 1936, *13*, 214,

ment reading and the actual moisture content as determined by the oven-drying method. A complete series of readings can be taken on one sample by making a test at intervals during the drying process. This curve will enable the readings on the instrument to be interpreted in values of moisture content on any further sample of the same material, but will not necessarily hold good for other materials, which, when dry, have a different Dielectric Constant. The method can be used for many materials on which the method of oven drying is inapplicable, calibration of the instrument being carried out by drying over a desiccating agent. The complete apparatus with a self-contained battery is contained in a portable instrument.

Boiling-points. When a pure liquid is in equilibrium with its own vapour at a definite temperature the vapour exerts a definite pressure, the vapour pressure. This fact may be stated otherwise—that the liquid boils at this temperature when subjected to this pressure. Thus vapour pressures and boiling-points are simply different statements of the same phenomenon, and the determination of one is coupled up with the determination of the other. Where a given temperature is stated as the boiling-point of a liquid the inference is that the corresponding pressure is standard atmospheric pressure. This is the usual meaning to be attached to the boiling-point, which may therefore be declared to be the temperature at which the vapour pressure of a liquid is equal to atmospheric pressure. This may be illus-trated simply by confining the liquid in the short arm of a J-tube over mercury and determining the temperature at which the mercury level in both arms is the same. This, then, is the boiling-point of the liquid under the pressure of the atmosphere.

In determining boiling-points with liquid in bulk, the temperature at which the liquid boils is not that required. In most cases this temperature is too high owing to the fact that the vapour bubbles begin below the sur-face and consequently are at a pressure greater than atmospheric. The liquid must have a perfectly free surface of evaporation ; consequently the temperature usually measured is that at which the liquid condensed on the bulb of the thermometer is in equilibrium with the surrounding vapour, when the thermometer bulb is in the vapour above the liquid surface. The vapour-pressure method of Ramsay and Young already described satisfies the necessary conditions for the determination of boiling-points. (See Vol. I, Chapter VIII, S. 5 :—Determination of Boiling-Point.)

SECTION 2: MANIPULATION OF GASES

Though reactions involving gaseous products are not so often met with in physico-chemical work as those in which we deal with solid and liquid constituents, nevertheless dexterity in the manipulation of gases is essential to the trained chemist. In working with gases to any reasonable degree of accuracy, great care is necessary both as regards the conditions of the experiment and general manipulation. The influence of temperature and pressure on the volumes of gases makes the regulation of these extremely important. To obtain comparative measurements it is essential to reduce all volumes to standard temperature and pressure, 0° and 760 mm. of mercury at 0°. The possibility of leakage or dilution of the gas with air makes the question of reaction-vessels, stopcocks, connecting tubes, &c., of paramount
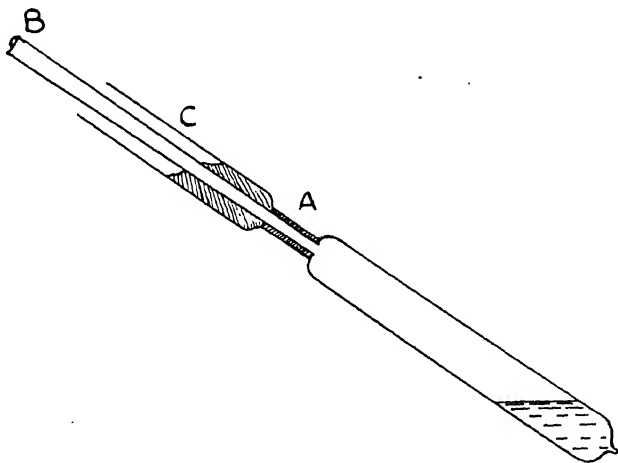
FIG. 9 (I *)

importance. Likewise, the solubility of gases in liquids must be taken into account when storing gases over liquids, as is usually done.

Connexions. Gas-tight connexions may be obtained by means of thick-walled rubber-tubing. The ends thus connected should be forced into the tubing till they meet inside the latter. The joint is fixed by twisting a strand of thin copper wire around each end of the rubber, using pliers. To render loose junctions gas-tight a form of mercury trap is sometimes fixed around the ends of the connexion. To connect pieces of quill tubing to tubing of larger diameter, the following method of Ramsay and Travers is convenient. The larger tube is drawn to a neck at A (Fig. 9 (I *)); a piece of thick-walled rubber tube is then forced into the neck, the quill tubing inserted, and the wide tube above the neck is filled with mercury,

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thus making the joint air-tight. Junctions are often made between ground-glass surfaces; such surfaces consist of a plug and socket made to fit one another and are usually fairly long so as to prevent leak. The ordinary design is shown at A (Fig. 10 (I *)). B shows a design which includes a mercury trap; the socket is turned out into a small reservoir into which mercury is poured; this type can be used for vacuum connexions. Fig. 11 (VI) C shows a simple type of seal [1] which may be employed without the use of ground stoppers. The glass tubes are first jointed by rubber and then a mercury seal fitted over this. Where possible, however, all junctions in gas-work should be sealed; a sealed glass junction gives absolutely no opportunity for leak, and the operation of sealing will be found simple with a little practice; where the apparatus does not require frequently to be taken apart, sealing the junctions will be well worth the trouble.
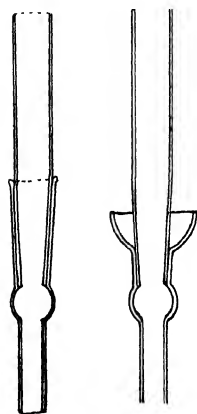
A   B
FIG. 10 (I *)

Stopcocks. The ordinary stopcocks used in opera-tion with liquids may also be used in gas-work if properly lubricated. The wide leading tubes in such work, however, cause a leakage in the stopcocks. Narrow-bore tubes are more to be recommended; a glass guard on each side of the passage, fitting the cock, prevents leak. The tube may be about 1 mm. in diameter. The openings for the tubes are usually bored at points not exactly opposite one another so that the bore runs diagonally through the glass (Fig. 11 (I *)). Three-way cocks are much used in gas-work; one kind has two leading tubes, one over the other, each with a corresponding diagonal passage through the cock to join the third tube at the other side (Fig. 11B (I *)); another type has the third tube at right angles to the

A   B
FIG. 11 (I *)

other two and the plug pierced in a T-shape. The first type is probably the better of the two. Four-way cocks are not generally used, as a combina-tion of a three-way and two-way cock may be used instead. A specially constructed six-way tap (Fig. 12 (I *)) has been used with success in con-nection with the supply of reagents for absorption and washing of gas during the process of analysis.[2] By the use of such a tap as shown in Fig. 12 (I *), , the bottles containing the solutions of pyrogallol, potassium hydroxide, ammoniacal cuprous chloride, and 1 per cent. sulphuric acid

[1] Donnelly, Foott and Reilly, *J. Soc. Chem. Ind.*, 1928, XLVII, 2, 1, T.
[2] Donnelly, Foott and Reilly, *Sci. Proc. Roy. Dub. Soc.*, 1928, *19*, 17, 168.

are connected to the apparatus, and unnecessary handling of the reagents avoided. The fifth arm of the tap is left blank for the introduction of any special reagent not in frequent use, whilst the sixth is connected to the two-way stopcock leading to the bell. The tap is so constructed that by rotating the plug the sixth arm may be connected in turn to each of the other five. The six arms are placed equidistantly around the barrel in three planes, two in the lower, three in the upper, and the sixth arm in the middle. No holes are drilled through the plug of the tap, but a ringed groove is cut opposite the centre arm. A second longitudinal groove, intersecting the central ring at right angles, is also cut long enough to connect the outer arms with the centre. This longitudinal groove is cut imme-
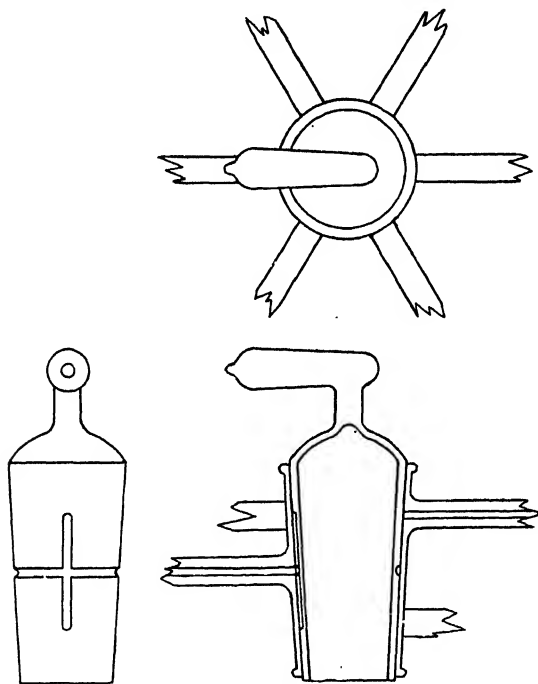
FIG. 12 (I *)

diately below a mark on the handle, so that the position of the plug may easily be seen. The cocks must always be lubricated with grease to prevent leak, and the cock may be protected by air-tight mercury cups at either end as with ground joints.

Leakage at the stopcock is a frequent source of error after it has been in use for some time, especially if the gas is kept at greatly increased or reduced pressures during analysis. The possibility of leakage can be minimized by using wide-diameter mercury-sealed stopcocks. The stopcock shown in Fig. 13 (I *), which has been found to be extremely satisfactory, has a hollow plug, 0·75 inch in diameter, at the centre, and can be sealed with mercury at the top and bottom. A hole drilled at the top of the plug allows mercury to run down the hollow centre into the well to seal

the lower join, and a cup round the top of the stopcock retains sufficient mercury to seal the upper join. When the plug is removed for greasing, the mercury collects in the well, and can be run off through the drain-cock provided for that purpose.

These large sealed stopcocks are only recommended for stopcocks which are continually in use, and where the gas undergoing analysis is subjected
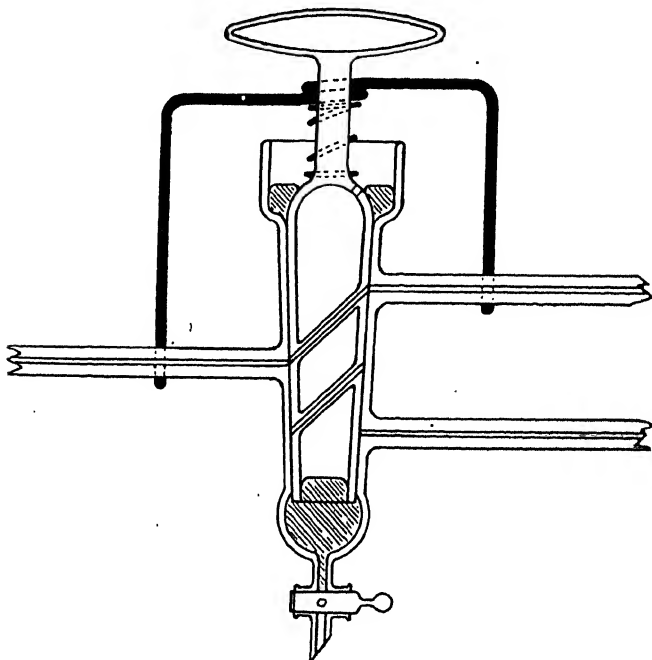

FIG. 13 (I *)

to big variations in pressure. Spring clips of the type shown in Fig. 13 (I *) are an advantage on all the stopcocks to keep the plugs in position. A suitable grease for the taps consists of about equal parts beeswax and vaseline, the proportions being varied according to the average temperature of the room in which the apparatus is situated.

Collecting and Storing Gases. For rough investigation of properties, a gas may be collected by upward or downward displacement of air in a gas-jar according to its density. Of course, this method does not secure a pure sample. To do this the usual method is to collect the gas over a liquid in a tube. Mercury is generally used in this process owing to its inactivity to most gases and their insolubility; with such acids or gases which might attack mercury some other liquid must be used. The gas tubes used should be small at their open ends to allow the thumb to cover the end when placing the tube in the trough. This type of tube is shown in Fig. 14 (I *). The tubes must first be filled with mercury free from air bubbles, then clamped and inverted, in the trough with the mouth under the mercury. When full of gas the mouth of the tube may be closed with

the thumb and removed, for analysis or storage ; the gas may be stored over mercury in such tubes for an indefinite time.

For the purpose of removing gases from such tubes the *siphon pipette* (Fig. 15 (I *)) may be employed ; this instrument consists essentially of a mercury reservoir A, a bulb B (for holding the gas), usually graduated so that it serves to measure volume, and a capillary tube C, bent as shown. The capillary should be of millimetre-bore tubing. The reservoir is connected to the pipette by means of pressure tubing wired on at either end ; a stopcock is interposed between the bulb and the end of the capillary. The reservoir is first filled with mercury and raised and lowered several times to drive out air bubbles. When the reservoir is raised the tube containing the gas is brought over the end of the capillary, the reservoir lowered and the gas drawn over into the bulb.

FIG. 14 (I *)

A convenient form of gas-sampling tube is shown in Fig. 16 (I *). It consists [1] of a tube of about 50 ml. capacity connected at the lower end,

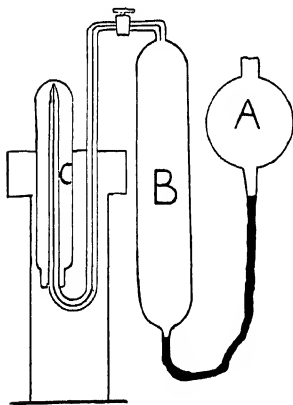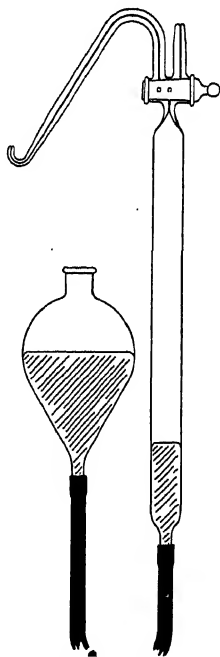FIG. 15 (I *)

FIG. 16 (I *)

with about 80 cm. of rubber pressure tubing, to a reservoir of mercury. The top terminated in a two-way capillary stopcock. One branch of this tap was cut to about 3 cm. long and tapered slightly so that it could be easily inserted into rubber pressure tubing. The other branch, about 15 cm.

[1] Donnelly, Foott and Reilly, *J. Soc. Chem. Ind.*, 1929, XLVIII, *6*, 38 T.

long, was drawn down to about 3 mm. towards the end and bent as shown. This bend enabled gas to be transferred directly from the sampling tube to the apparatus for analysis, or into test-tubes over mercury.

For collecting and storing larger volumes of gas, large gas-holders must be employed. For volumes of about 250 ml. the type shown in Fig. 17 (I *) may be employed. The gas, from a pump or directly from a reaction vessel, is led by means of the capillary tube *d* into the vessel A and allowed to collect there; this vessel is connected with the gas-holder by means of a capillary tube and stopcock. The gas-holder is originally filled with mercury, the bottom level of which is lower than the bottom level in A. By turning the stopcock the gas will flow into the gas-holder; the mercury in the latter flows away through the tube at bottom.
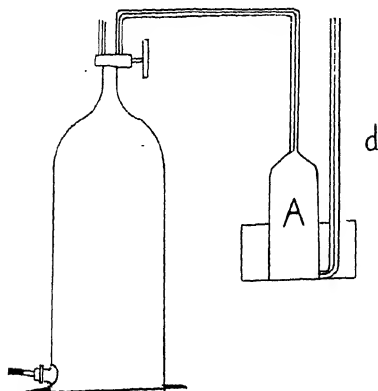
FIG. 17 (I *)

Large bottles, such as used for storing solutions, may be used for storing gases; the bottle is first filled with water, if this liquid can be used, as the volume required is so large. The gas is led in at the top and the water allowed to flow away through the tube at the bottom (Fig. 18 (I *).

For collecting gases evolved from mineral springs in large quantities, Ramsay and Travers employed the method illustrated in Fig. 19 (I *). A large tin vessel was fitted with stopcocks and rubber connections at each

FIG. 18 (I *)

Floor of Tunnel
Water
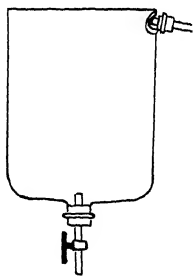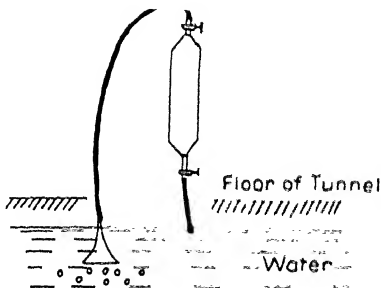
FIG. 19 (I *)

end as shown; a funnel was attached to the rubber at one end; the apparatus was first filled with water, then the water allowed to flow away through one tube while the gas is led in via the funnel at the top.

For the introduction of gas-free reagents or gas samples into a reaction vessel the mercury seal is often employed. The rubber tip on the delivery tube of the sample vessel, under mercury, is pressed against the top of the tube communicating with the interior of the reaction vessel. Where it is not for other reasons undesirable a drop of octyl alcohol on the

rubber tip is often beneficial in avoiding the introduction of minute bubbles.[1]

Measurement of Volume. Practically all quantitative work on gases depends on volume measurements; the actual measurement usually made is, therefore, that of the level of a liquid meniscus; this measurement may be made with the eye or with an optical instrument, according to the needs of the experiment; most of the errors possible have already been discussed. The mirror scale may be used for the measurement, as in reading a barometer or manometer; the usual method is to confine the gas in a tube previously graduated, the graduations may be etched on the glass, and the meniscus level read with the eye or a reading telescope. To give any meaning to a measurement of gas volume, the corresponding pressure and the temperature must be known. The volume is usually read at atmospheric pressure by equalizing the levels of the liquid inside and outside the gas tube; the latter is then accurately read from a barometer. Where the levels cannot be adjusted, the difference in level must be determined and added to or subtracted from the barometric height. If the liquid in contact with the gas has an appreciable vapour pressure at the temperature of the experiment, a correction for this must be applied; also where a difference of pressure is being read the temperature of the liquid column must be taken into account. The correction for capillarity must also be applied where there is inequality of bore; the table for this correction in the case of mercury has already been given.

The experimental pressure is usually reduced by Boyle's Law to a standard of 760 mm. of mercury at 0°.

The temperature of the gas is taken as being that of the surroundings; it is not usual, except in very accurate work, to surround the gas with a constant-temperature jacket. The volume of the gas is reduced to the volume it would occupy at 0°.

The true volume of a gas is thus determined from the equation

$$V_0 = \frac{V' \times B}{273 + t} \times \frac{273}{760}$$

where V' = observed volume

B = corrected barometric height

t = observed temperature

The Hempel gas burette, illustrated in Fig. 20 (I *), consists of a 100 ml. burette graduated in fifths of a millilitre, provided with a short capillary at the top and closed by a rubber connexion and stopcock. It is connected at the bottom by rubber tubing with a levelling reservoir, similar to the burette. To measure volume the reservoir is filled with liquid and raised so as to drive all gas out of the burette and fill it with liquid; the burette is then connected to the gas supply, the reservoir lowered, and the gas drawn into the burette. The tube is then closed and the gas measured under atmospheric pressure by levelling the liquid surfaces in the burette and reservoir. The burette may be surrounded with a water jacket to keep a known constant temperature.

[1] *Ind. Eng. Chem.*, N. Ed., 1937, *15*, 21, 474; Sendroy, *Ind. Eng. Chem. Anal.*, 1937, *9*, 190.

A slight modification of this .method is the constant-volume method. The gas tube or burette is not completely graduated, but its volume to a certain mark is known ; the meniscus is brought to this mark by adjusting the pressure ; the reading of the latter is taken and the volume under standard conditions calculated.
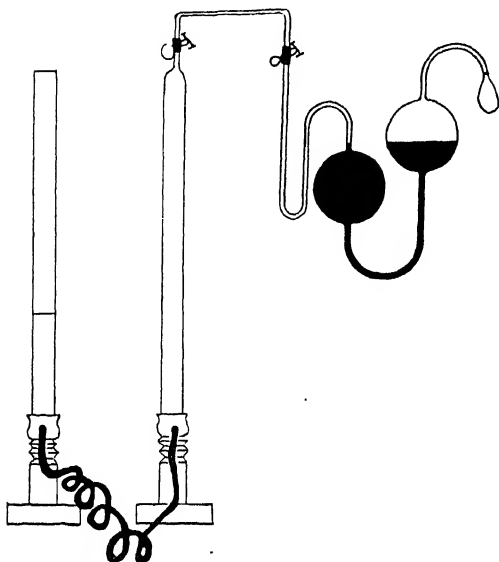
An accurate method of estimating volume, but one not often used, is that of displacing an equal volume of mercury and weighing the latter. From the known density the volume may be calculated. This method may be used for the calibration of vessels to be used in volume measurements.

The Measurement of Gas Flow in Pipes by the Hot Wire Anemometer. The fact that a fine platinum wire heated electrically undergoes a change in resistance due to cooling when immersed in a stream of fluid, has been utilized as a method of practical anemometry. Hot wire anemometers based on this principle have been described by Morris [1] and later by Thomas,[2] who first applied them to the

FIG. 20 (I*)
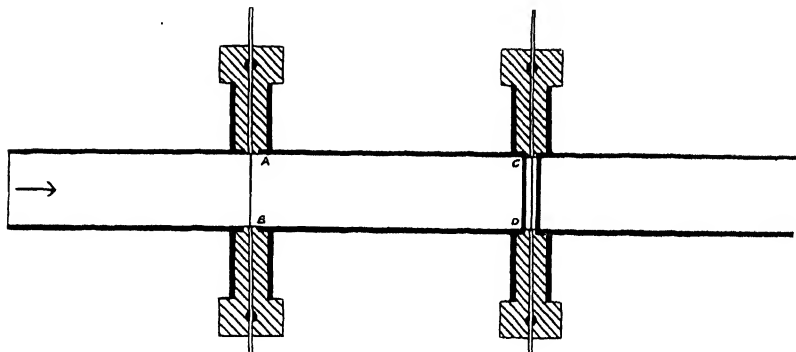
FIG. 21 (1*)

measurement of velocity of fluids in pipes. The designs favoured by these workers resemble a bolometer arrangement, the cooling produced by a stream of fluid causing a change in resistance of a fine platinum

[1] Morris, Eng. Pat. 25923/1913.
[2] J. S. G. Thomas, *Phil. Mag.*, 1921, *39*, 505.

wire which composes one arm of a Wheatstone bridge. The principle has been applied by Thomas to the measurement of the flow of gas in a tube or pipe. His arrangement is indicated diagrammatically in Fig. 21 (I *). Two fine platinum wires, the one AB exposed, the other CD shielded, were inserted as shown, in the tube through which a current of air or other gas flows. The wires AB and CD were cut from the same sample of platinum, and were aged by the passage of a suitable electric current for some hours. The lengths of the wires were as nearly as possible equal to the diameter of the flow tube, and they were located at such a distance apart that disturbance of the flow set up by the presence of CD produced no effect at AB. The two wires constitute two arms of a Wheatstone bridge, the remaining arms of which are formed of manganin resistances from a resistance box. The battery and galvanometer were connected to the bridge in the usual way and by means of a rheostat in series with the battery the current in the bridge was maintained constant. Usually the resistances of the other arms of the bridge were about 2,000 ohms, those of the wires AB and CD being about 0·5 ohms for the heating current employed, so that almost the whole current in the bridge when balanced passes through the platinum wires. A bridge employed in this manner is a constant current bridge, giving maximum sensitiveness in accordance with Maxwell's rule, and with the maximum generation of heat in the sensitive branch.

The anemometer was calibrated by passing a stream of gas from a gasometer through a gas-meter in series with the anemometer flow tube. A number of fine copper gauzes were inserted into the mouth of the flow tube, so as to effect distribution of the current of gas across the section of the tube. The bridge was first balanced with zero flow of air, the air current now passed through the tube and the deflection of the galvanometer was observed on adjusting the current to its initial value. The drop of potential across the shielded wire was next determined, and the bridge restored to balance by adjusting the resistance in the fourth arm of the circuit, the electric current being maintained constant throughout. The temperature of the air stream and of the air in the meter and the barometric pressure were noted—the readings of gas volumes being reduced to 0° and 760 mm. pressure. The disturbing effects which might affect the anemometer readings have been thoroughly investigated by Thomas, and these together with variations and the use of the anemometer with gases other than air are very fully described in his original paper. A hot wire anemometer of quite a different type is described by Teegan,[1] and has been applied to the measurement of slow streams of air in pipes.

Into the filament circuit of an ordinary R-type thermionic valve a fine platinum wire (2·5 cm. long and 0·010 cm. diameter)* was placed. This wire was stretched across a cylindrical tube 5 feet long and 2·5 cm. diameter. The method of inserting the wire is indicated in Fig. 22 (I *). The ends, a, b, of the wire were affixed by the smallest possible amount of solder to two brass screws fixed diametrically with respect to the section of the tube. Two stout insulated copper wires were attached to these screws, and were connected, as indicated, into the filament circuit of the valve,

[1] J. A. C. Teegan, *Phil. Mag.*, 1926, 1117.

which also contained a reliable ammeter A and rheostat R (Fig. 22 (I *)). The tube containing the platinum wire was clamped horizontally, and was securely connected by a pipe, of the same diameter, to a gasometer of 8 cubic feet capacity. The gasometer was fitted with ball-bearing pulleys, and its rate of fall was found to be exceedingly uniform, so that quite small air-streams could be produced and measured with accuracy.

When a stream of air cools the platinum wire, its resistance diminishes, and a greater p.d. is therefore applied to the valve filament. The resulting increase of filament temperature causes a corresponding increase in the current flowing in the anode circuit BG. The anode current variations can be utilized as a measure of the velocity of the air stream passing the wire. The grid and anode are joined and sufficient voltage applied for saturation, and the normal anode current for zero gas flow is balanced by
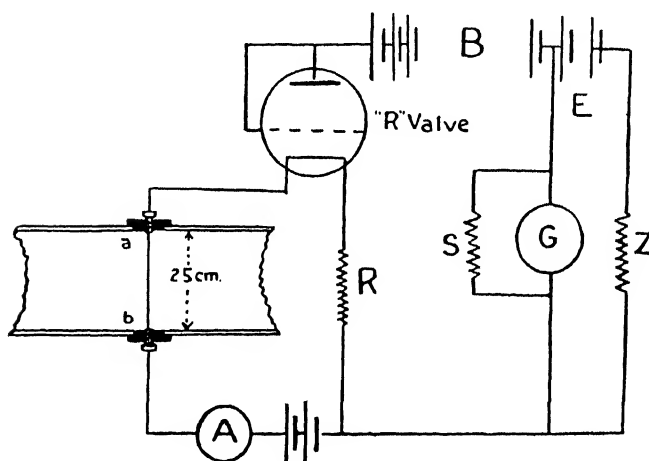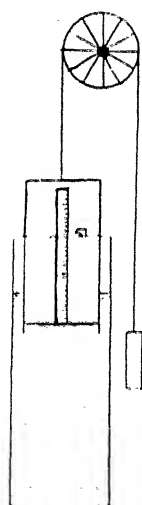
FIG. 22 (I *)   FIG. 23 (I *)

the shunt current EZ. The galvanometer used in these experiments had a sensitivity of 300 scale divisions per micro-amp.

Over a range of velocity of 0·7 inch to 5 inches per second, the calibration curve of the anemometer is linear.

Gas Meters. For the measurement of large quantities of gases in technical practice, various types of apparatus are employed. That illustrated in Fig. 23 (I *) is constructed on the principle of the gasometer. The gas is stored in a holder which is balanced by a weight. To remove gas the weight is adjusted the necessary amount, the holder sinks and the gas is expelled. The amount of gas is read off on the scale by means of a pointer. The scale must previously be calibrated, using known volumes of gas.

In measuring the quantity of gas passing through a system, gas meters are employed. These may be divided into two types, the wet meter and the dry meter. The wet meter consists of a cylindrical drum divided into

four spiral compartments (Fig. 24 (I *)). The drum rotates under the pressure of the gas, emptying a drumful of gas into the casing and pipes. Each rotation of the drum supplies an amount of gas equal in volume to twice the upper half of the drum. The number of revolutions of the drum is registered on a dial, showing the volume of gas passed. A gauge glass with a fixed water-level mark is provided, as variations in the level influence the dial indications.

The dry meter consists of a box divided into two compartments by means of a diaphragm ; the latter consists of metal attached to the wall of the box by an annular ring of flexible leather. The gas is led into one compartment and forces the diaphragm to the other compartment of the box ; the latter is connected to the gas burners ; when this compartment is empty a mechanical slide-valve arrangement changes the connexions, empty compartment to the supply, and full compartment to the burners, and the process repeats itself ; the number of movements of the diaphragm is automatically recorded.
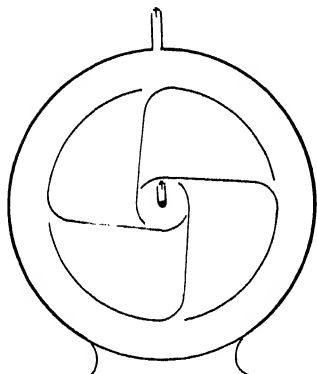
FIG. 24 (I *)
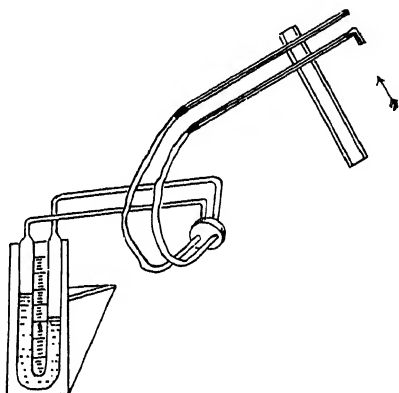
FIG. 25 (I *)

Flow Meters. Other meters used depend on the velocity of flow of the gases ; they do not measure quantity directly, though the latter may be calculated from the diameter of the pipe. Of these the Pitot tube (Fig. 25 (I *)) is commonly used. This consists of two glass tubes of about 0·1875-inch internal diameter ; one is bent at right angles and is placed so that it opposes the gas movement. These are connected by rubber tubing, through a ' reverser ', with a U-tube manometer which may be inclined to increase the accuracy. One arm registers merely the pressure of the gas, the other registers the pressure plus the force of impact ; the difference between the arms of the U-tube is approximately proportional to the square of the velocity.

The Thomas Electric Gas Meter. In this meter heat is given to the gas by means of an electrically heated coil, so that the difference of temperature, before and after the coil, is fixed : the specific heat of the gas being known, the electrical energy required to heat the coil is a measure of the quantity of gas passing. Electrical thermometers are used and fixed

to maintain 2° difference of temperature. The meter is independent of temperature or pressure changes.

Other meters are constructed depending on the pressures produced by the viscosity of the gas in flowing through capillary tubes.

Reaction between Gases and Metals. The reaction between gases and metals is of both theoretical and technical importance in chemistry. From the physico-chemical aspect we are more concerned with those reactions where no chemical reaction occurs between the metal and the gas as judged by final products. In many catalytical processes, in the production of high vacua and in many metallurgical processes these gas-metal equilibria are of great significance. The available data on the subject has been collected and critically considered by Smithells,[1] who has conveniently subdivided the subject under three headings, (a) adsorption (see Chapter V, S. 2), (b) diffusion, and (c) solution. The experimental method generally employed for adsorption phenomena with metals and gases involves the use of the Pease apparatus as modified by Benton and White.[2] It consists of a 50-ml. adsorption bulb connected to a mercury ' cut-out ' and to a Topler pump, to a manometer and to a tap. This latter is used for the introduction of gas to a measuring cylinder of known volume. The volume of the ' dead-space ' in the adsorption bulb is determined by means of helium, as this gas is not adsorbed by metal at ordinary atmospheric temperature. The heat of adsorption can be estimated by the method of Maxted.[3]

The apparatus used in experiments on diffusion of nascent hydrogen is generally simple.[4] It consists of a metal tube connected by glass tubing to a manometer and to a diffusion pump. In a beaker is placed a dilute solution of acid or alkali. For anode a platinum plate is used and the metal tube is connected to the negative terminal of the battery. The apparatus is evacuated and the electric circuit completed. The amount of hydrogen diffusing through the metal tube is determined from the changes of pressure registered. Smithells and Ramsley [5] have described a sensitive form of apparatus, using a McLeod gauge, and the defects of older types of apparatus have been removed.

The solubility of gases in metals is determined by placing a known weight of metal in a gaseous atmosphere at a known temperature and pressure until equilibrium is obtained and noting volume of gas adsorbed. Sievert's apparatus,[6] or a modification of it, is generally employed. A special type of reaction bulb is employed by Bircumshaw.[7]

[1] *Gases and Metals*, Chapman & Hall, London, 1937.

[2] *J. Amer. Chem. Soc.*, 1930, *52*, 2325.

[3] *J. Chem. Soc.*, 1930, 2093 ; cf. also Maxted and Moon, *Trans. Far. Soc.*, 1936, *32*, 1375.

[4] Borelius and Lindblom, *Ann. Physik.*, 1927, *82*, 201 ; cf. Smithells, *l.c.*

[5] *Proc. Roy. Soc.*, 1935, *150*, 172.

[6] *Z. Metallk.*, 1921, *21*, 37 ; cf. also Toole and Johnson, *J. Phys. Chem.*, 1933, *37*, 331.

[7] *Trans. Far. Soc.*, 1935, *31*, 1439.

In general the various constituents of a gaseous mixture are determined by absorbing each constituent in a suitable reagent and observing the diminution in volume produced. Where the gas is unabsorbable, it is usually burned or exploded and the volume determined from the circumstances of the reaction. Liquid reagents are generally used in the absorption, as the reaction more easily occurs, and more intimate mixing is possible than with solids. They incur the disadvantage of dissolving the other gases present as well and in different proportions. In this way the use of solid reagents probably leads to the most accurate results.

Bone and Wheeler's Apparatus. The general character and arrangement of the various parts of the apparatus will be readily understood, with the aid of the accompanying figure (Fig. 26 (I*)). It comprises three parts, viz.: (1) water-jacketed measuring and pressure tubes, communicating through the glass tap with a mercury reservoir as shown; (2) an absorption vessel standing over mercury; (3) an explosion tube. All the connexions between these vessels are of capillary bore throughout, with suitable glass taps where necessary. The figure also shows how connexion is made between the measuring tube and the special 'sample tube' whenever the latter is employed for the introduction of the sample under consideration. The

FIG. 26 (I*)

sample can also be introduced into the apparatus from an ordinary test-tube under the wide open end of the absorption vessel, which has been previously filled with mercury. Before commencing an analysis the whole of the apparatus, including the connexions, is completely filled with mercury. For measurement purposes the gas is brought to a certain 'constant-volume' mark in the measuring tube, by suitable manipulation of the
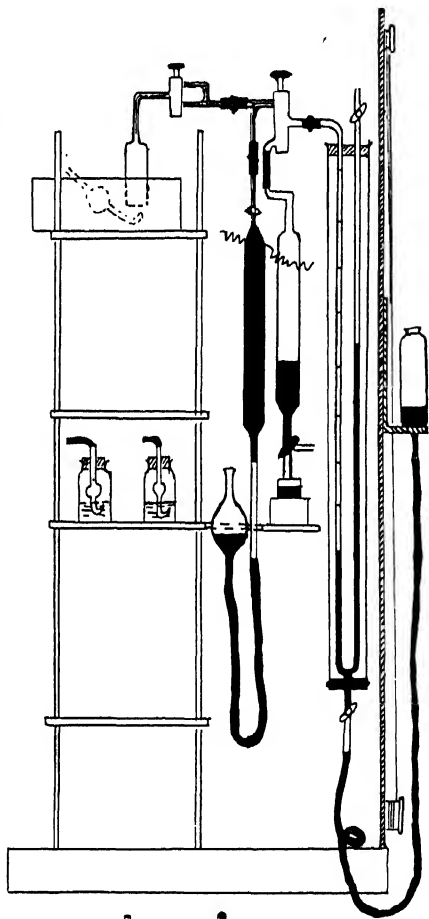
mercury reservoir and the tap ; and its pressure read off on the pressure tube. The method now generally used in manipulating the gas is to employ the direct pressure of the water main and the force from a suction pump to raise and lower the mercury. The mercury reservoir is clamped so that the level of the mercury is near the bend of the U-tube, or a little above it if the pressure of the water is insufficient to force the mercury over into the bell from the lower level. The top of the reservoir is closed by a two-way stopcock, one side of which is connected direct to the water main, and the other, through a mercury trap, to the suction pump. Small tapered file nicks in the sides of the holes in the plug of the stopcock facilitate the fine adjustment of the mercury level in the gas-measuring burette. When the stopcock is in the 'off' position, a groove in the plug connects the water main to the suction pump, which reduces the pressure and provides a stream of water for washing the mercury in the trap. A drain-cock, included at the lowest point between the mercury reservoir and the gas measuring burette, enables the system to be easily emptied of mercury [1] (Fig. 27 (1*)). The measuring and pressure tubes are surrounded by a water-jacket, and their inner surfaces are kept moist with very dilute sulphuric acid (1 in 20) as a precaution against the accidental fouling of the measuring tube with alkalis, and to eliminate the influence of water vapour upon the gas measurements, the various pressures representing those of the dry gas under examination. The tap closing the upper end of the pressure tube is connected with it by means of stout rubber pressure tubing (not shown), which gives a perfectly tight joint with sufficient elasticity to prevent fracture in case the mercury in the pressure tube is inadvertently allowed to run up the tube with unusual velocity. The tap in question also allows of the vacuum being easily made in the pressure tube whenever necessary. To prevent breakage in allowing the mercury when under vacuum to ascend the gas burette too quickly, a modification may be made by introducing a restriction of about 1 millimetre diameter in the form of a jet between the water main and the mercury reservoir. To prevent 'whistling', the jet should be pointed in the opposite direction to that in which the water is flowing. Between this jet and the main a T-piece is inserted to supply water to the cooling jacket around the gas burette, and a constriction included to control the rate of flow.

Flanged joints should be inserted in the apparatus where necessary to permit of the easy removal of parts for repairs, and should include one between the gas measuring burette and the stopcock adjoining it. The best sealing material for these joints is gold size.

The arrangements for the various 'absorptions' are simple. Instead of using a number of large absorption vessels, each containing a particular reagent which is used unchanged many times over in successive analyses, all the absorptions are carried out over mercury in the one absorption vessel, in each case with a comparatively small volume of the particular reagent, which is always used fresh and is at once discarded after use.

To facilitate the introduction of the various reagents, and the rinsing out of the absorption vessel with water or dilute sulphuric acid *in situ* between each successive reagent, the wide (open) end of the vessel is immersed

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[1] Donnelly, Foott and Reilly, *Sci. Proc. Roy. Dub. Soc.*, 1929, *19*, 17, 165.

under the mercury in a trough, whilst the top terminates in a capillary three-way tap. One of the parallel branches of this tap communicates,
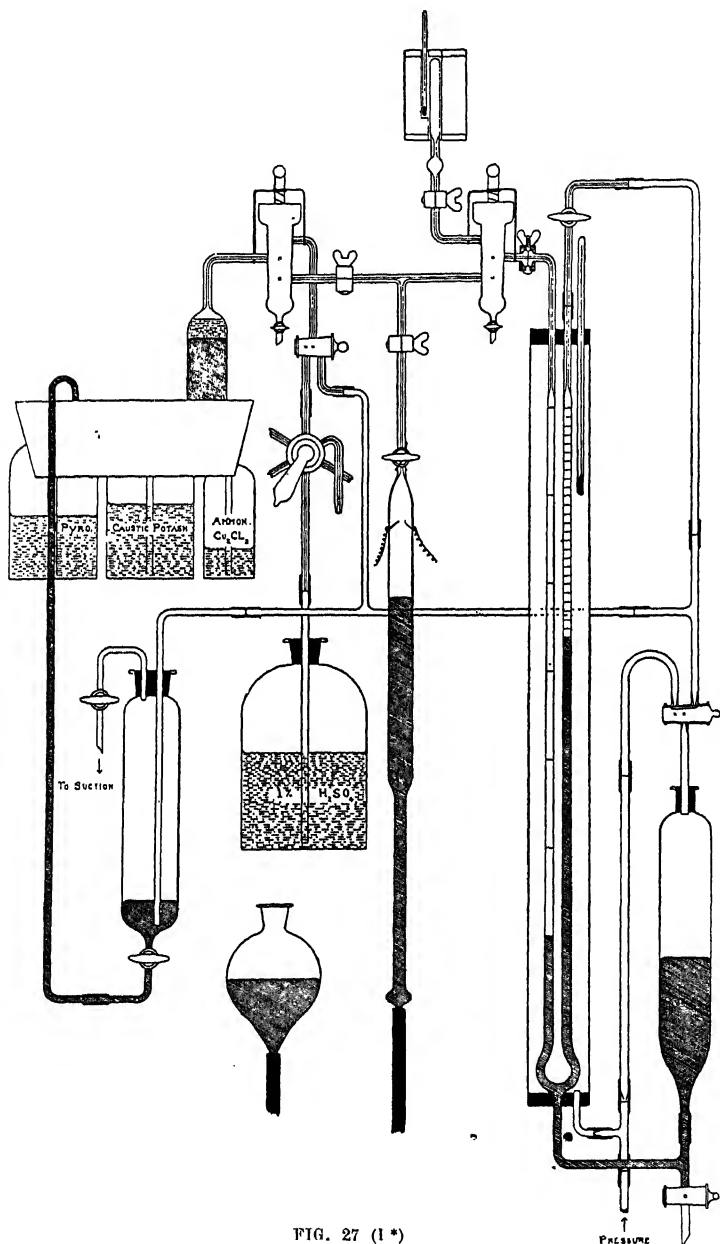

FIG. 27 (1 *)

through a stout rubber joint, with the measuring vessel, and the other with a water pump, a large bottle being inserted between the pump and the absorption vessel to serve as a trap for either the mercury or the reagent

which is being discarded after use.   The insertion of a tap between the pump and the bottle obviates the necessity of the continuous exhaustion of the latter, a single exhaustion at the outset of an analysis being all that is required.

From 2 to 5 ml. of the particular reagent to be used is introduced into the absorption vessel (previously filled with mercury) by means of a suitable pipette, from below the surface of the mercury in the trough.   Any minute bubble of air accidentally introduced with the reagent can be got rid of by cautiously opening the branch of the three-way tap leading to the above-mentioned exhausted bottle ; the simple device allows of the complete withdrawal of the reagent after use, without taking down the absorption vessel, and also of the rinsing out of the latter *in situ* with water, or dilute sulphuric acid, before the next reagent is used.
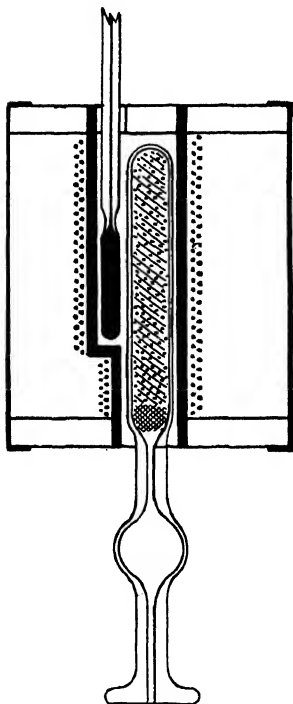
In this way, using small quantities of each successive reagent, always in a fresh condition, and washing the vessel out *in situ* between each reagent, a series of absorptions can quickly be carried out without disturbing a single connexion in the apparatus.   It may also be added that long experience has proved that the use of such reagents as a solution of bromine (in potassium bromide—see below) for the absorption of unsaturated hydrocarbons is unattended with difficulty.   The above apparatus is especially suitable for accurate work.

The method of using copper oxide for estimating hydrogen in the presence of hydrocarbons was first applied by Jäger.   The apparatus described below consists of a silica tube, 6 cm. long by 1 cm. in diameter, closed at one end, and lightly filled with a mixture of equal parts of short fibre asbestos and fine copper oxide.[1]   The other end is drawn off, expanded to a bulb, and connected in a vertical position above the apparatus to the two-way stopcock at the top of the gas burette by a flange joint.   A small electric furnace, wound so that the full pressure of the electric main gives a temperature of 600°, is placed around the silica tube.   A switch is arranged to give an alternative circuit through a lamp of a resistance chosen to give a maximum furnace temperature of 270°.   One advantage of having alternate circuits is that by using the full current the furnace may be quickly heated to the desired temperature of 280° before switching in the resistance (Fig. 28 (I*)).

FIG. 28 (I*)

When the analysis has reached the stage where the hydrogen is to be estimated, the sample is stored in the explosion chamber, while the copper oxide tube, which has already been heated to 280°, is evacuated.   The

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[1] Donnelly, Foott and Reilly, *Sci. Proc. Roy. Dub. Soc.*, 1929, **19**, 171.

gas-measuring burette is employed as a pump to expel the air from the oxide tube into the adjacent bell. The evacuation is usually complete after five or six ' strokes '. The sample is then removed from the explosion chamber to the gas burette, and allowed slowly to enter the copper oxide tube. With the furnace in a vertical position, the bulb adjoining the copper oxide tube prevents droplets of moisture or mercury, which may have become trapped in the capillary tubing, from being carried into the hot oxide tube, and also enables the water formed by the combustion to be removed. As the copper oxide tube is large enough to contain the whole of the gas sample, combustion of the hydrogen is complete in a very short time, after which the copper oxide tube is again evacuated and the contraction in the volume of the gas sample measured. On completion of the analysis, the copper oxide tube is filled with oxygen, and the temperature of the furnace raised to 600° to reoxidize the copper. A pocket in the electric furnace allows a thermometer to be inserted alongside the copper oxide tube, so that the temperature may be watched during the combustion of the hydrogen.

Simple Apparatus. Where gas analyses are not being continually performed a special apparatus is not always necessary. A known volume of the gas may be confined over mercury in a trough and a small quantity of the absorbing solution introduced by a thumb-tube; the remaining gas is then transferred to a gas-measuring burette by means of a siphon pipette, and the volume measured.

A convenient form of absorption pipette is represented in Fig. 29 (I*). The instrument uses the principle of the siphon pipette to draw over the gas; the tubes are put into communication by the stopcock and the gas drawn through the reagent, which is placed on top of the mercury in the pipette; when absorption has occurred, communication with the pipette is secured and the gas expelled to a measuring vessel.
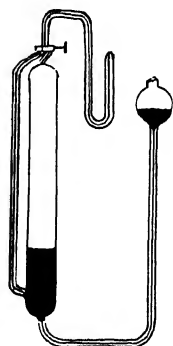
Hempel's Apparatus. This is much used in both laboratory and technical work; the instrument is illustrated in Fig. 20 (I*). The measuring tube holds 100 ml. and is calibrated throughout.

FIG 29 (1*)

The absorption apparatus consists of two bulbs as shown. One is completely filled with the reagent and the other partially so. It is connected to the burette by means of a narrow tube. The levelling tube, which is open at the top, is connected at the bottom to the bottom of the measuring tube. This may be surrounded by a water jacket to obtain a steady temperature. In working, the tube is filled with water by raising the levelling tube; it is then connected to the gas-holder and by lowering the levelling tube the gas is drawn over into the measuring vessel. The connexion with the narrow tube is then made and by raising the levelling tube the gas is forced into the absorption apparatus, driving the liquid into the second bulb.

The connexion with the narrow tube is then closed and the stopcocks are removed. A couple of minutes, during which the pipette is gently agitated, usually suffices for absorption. The connexion with the burette

is again made and the gas withdrawn and measured. By means of a second, third, or fourth pipette, each filled with different reagents, various constituents of the gas can be removed.

Orsat Apparatus. This apparatus is much used in technical practice. Fundamentally it is not unlike the Hempel apparatus. It consists of a levelling bottle (Fig. 30 (I*)), burette, enclosed in a water-jacket, and

pipettes P′, P″, and P‴ (not marked in fig.). P′ is the vessel on the left-hand side, P″ in centre and P‴ to the right. P′ is filled with caustic potash solution, P″ with alkaline pyrogallol solution, and P‴ with cuprous chloride solution. These reagents absorb respectively carbon dioxide, oxygen and carbon monoxide. Exactly 100 ml. of gas are confined originally in the burette, the levelling bottle is raised and the tap with P′ opened. The gas is forced into P′ and may be withd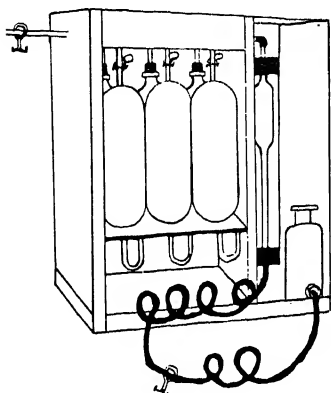rawn and forced in again several times to hasten absorption. Finally, the tap is closed and the volume measured. In the same way the oxygen is absorbed in P″ and the carbon monoxide in P‴.

FIG. 30 (I*)

Winkler's Apparatus. For absorption analysis in general, Winkler divided the gases into seven groups, according to the reagent used to remove them. His classification is as follows :

(i) Sulphuric acid, 1·7 specific gravity ; ammonia, higher oxides of nitrogen (N_2O_3, N_2O_4)

(ii) Potassium hydroxide : chlorine, hydrogen chloride, cyanogen, prussic acid, sulphur dioxide, sulphuretted hydrogen, silicon tetrafluoride, carbon dioxide

(iii) Silver nitrate : phosphine, arsine, stibine

(iv) Pyrogallol : oxygen, ozone

(v) Cuprous chloride : carbon monoxide

(vi) Acid ferrous sulphate : nitric oxide

(vii) Unabsorbed : hydrogen, methane, ethylene, ethane, nitrous oxide, nitrogen, carbon oxysulphide, and the ' noble ' gases

Ambler's Apparatus. A simple type of apparatus has been described by Ambler [1] for the analysis of samples of gas of about 1 ml. which can be analysed with an accuracy of about 1 per cent.

In the analysis of samples of gas of about 1 ml., causes of error become important, which would be quite negligible for larger samples. The chief of these are : (1) Rubber connexions, which may lead to (a) small air-locks at the joints, (b) small leaks when the rubber becomes old. (2) Physical solution of the constituent gases in each reagent, as distinct from the specific chemical absorption for which the reagent is used. (3) The limiting error of reading, which is proportionately greater for smaller samples. The apparatus has been designed to reduce such effects to a minimum :

[1] *Analyst*, 1929, *54*, 517.

(1) Rubber connexions have been abolished. (2) The volume of absorbent reagent has been diminished. (3) The sensitiveness of reading has been increased.

A portable form of this apparatus has been described by Ambler in the *Analyst*.[1] This modification will be described. A diagrammatic sketch is shown in Fig. 31 (I*). The central glass unit consists of a vessel in which the gases are measured, fused to another vessel in which they are absorbed or burnt.

In the full-size apparatus the mercury reservoir R_1 is raised and lowered by means of a cord passing over a pulley, and a counterpoise sliding on a metal rod; in the portable design this is eliminated by the introduction of the tap T_2 between the reservoir and the measuring burette; the reservoir is provided with two rests, at levels near the top and the bottom of
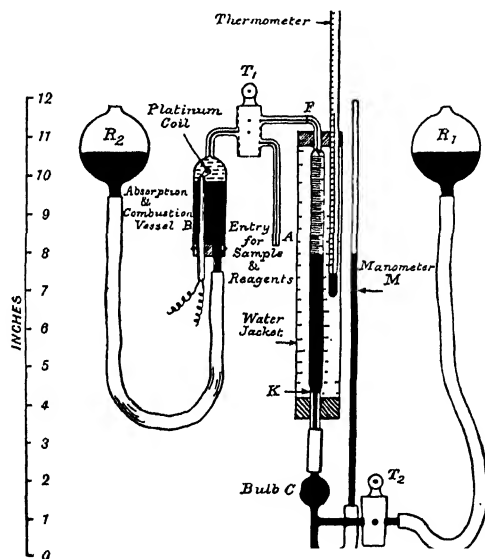
FIG. 31 (I*)

the manometer scale. To adjust the mercury level in the measuring burette, R_1 is placed on one of these rests, with the tap T_2 closed. T_2 is now opened and the mercury rises or falls in the burette until the required position is attained, when the tap is closed. With a good tap a fine adjustment is obtained without difficulty.

The experimental procedure is as follows: (1) The gas sample (up to 10 ml.) is introduced into vessel B from A.

(2) The tap T_1 is reversed and the sample transferred to the measuring vessel. By running mercury to the marked point F, the measuring vessel is sealed against leak out of gas or leak in of air.

(3) A quantity of the appropriate absorbent is introduced into B from A.

(4) The gas is transferred to B where the absorption takes place.

(5) The gas is transferred back to the measuring vessel; as soon as the

[1] 1929, *54*, 517; see also *J. Sci. Inst.*, 1931, *8*, 369.

absorbent liquid has reached the left-hand side of the tap, the latter j
reversed and the reagent driven out through A ; the tap is then reverse
again and the gas followed up with mercury to the mark F as before.

The measuring vessel consists of a burette of 10 ml. capacity, graduate
in tenths of a millilitre. Close below the 10-ml. mark the burette narrow
to a bore of 3 mm., and a mark K is etched round this narrow part.

It is seen that both varying volumes and varying pressures can b
measured at constant temperature.

Where maximum precision is not required, the quickest procedure, an
the simplest to compute, is to level the mercury in the burette with th
mercury in R_1, which is held in the hand by the side of the burette, an
to read the volume.

This method is suitable for all ranges of composition and gives result
accurate to within 0·5 per cent on the total gas. The limit on the precisio
is the approximate way in which the mercury is levelled and the gas brough
to atmospheric pressure. The most common method for precise levellin
is to incorporate by the side of the burette a tube of the same bore, ope
to the atmosphere. This, however, besides introducing possible paralla
errors, would involve a larger water-jacket and a greater weight of mer
cury. (Parallax could be eliminated by the introduction of two such ope
tubes on either side of the burette, but this would still further increas
the bulk and weight.)

The modification of the constant-pressure method, which has been foun
the most satisfactory for precision work, is to bring the gas in the burett
to approximately atmospheric pressure (say, within 2 mm.), to measur
this pressure, and then correct the observed volume to atmospheric pressure

Manipulation is very simple and quick ; when the approximate levellin
has been made, the tap T_2 is closed and the burette and the manomete
read. The pressure in the burette is then equal to the atmospheric pressure
plus the difference between the manometer reading and the reading of th
manometer when the burette is filled to the same mark at atmospheric
pressure. Call this difference ΔP cm.

The manometer readings corresponding with the different burette read-
ings at atmospheric pressure are a constant of the instrument, determined
once and for all by measuring a few points with the tap T_1 removed. These
are then graphed and form a straight line. (It is to be noted that this
procedure eliminates any differential capillarity effects.)

The correction to the burette reading is applied as follows :

Let B be the atmospheric pressure, W the vapour pressure of water at
the temperature of the experiment, V the burette reading, i.e. the volume
of the moist gas at the experimental pressure, V_A what the burette reading
would have been if the mercury had been levelled to exactly atmospheric
pressure. Then

$$V_A = V \times \frac{B - W + \Delta P}{B - W}$$

i.e.
$$V_A - V = V \times \frac{\Delta P}{B - W}$$

If ΔP is not greater than 1 cm., then any deviation of B — W fro

the average approximate figure of (76 — 1) = 75 cm. will not affect the correction sufficiently to introduce an error of more than 0·1 per cent on the total gas. In practice, ΔP does not exceed 2 mm. ; the magnitude of the correction is, for 1 mm. of ΔP,

$$V \times \frac{0·1}{75} = V \times 0·00133 \text{ (i.e. 0·13 per cent of V)}$$

The vessel B may be fitted either with spark gap or with platinum spiral for the combustion of hydrogen and other combustible gases. The instrument illustrated here is fitted with platinum spiral. This arrangement is of wider applicability than the spark gap, and also saves the extra weight and bulk of an induction coil. Gas mixtures containing more than 10 per cent of hydrogen or 3 per cent of hydrocarbons should be diluted with air before combustion. Where larger proportions than these are to be regularly dealt with, the bulb with spark gap, as shown in the description of the earlier apparatus, may be preferred.

The platinum coil [1] consists of about 1·5 cm. of wire of 0·125 mm. diameter. Current can be supplied by a 4½-volt dry battery controlled by a 3-ohm rheostat.

Winkler's Classification of Reagents can only be accepted as a general classification, and for various mixtures special devices must be adopted to obtain selective absorption. As general reagents for absorption in any of the above types of apparatus the following solutions may be employed :

Reagents

Potassium Hydroxide for Carbon Dioxide. 500 grams of potassium hydroxide dissolved in 500 ml. of water.

Pyrogallol for Oxygen. 30 grams dissolved in 100 ml. of water. Portions of the solution are added to the potassium hydroxide solution left from the carbon dioxide absorption. Pyrogallol keeps better if slightly acid, but must have three to four times its volume of concentrated potassium hydroxide for absorbing oxygen. Pyrogallol, if partly exhausted, is liable to evolve carbon monoxide.

Ammoniacal Cuprous Chloride. Take 15 to 20 grams cuprous chloride, add half the weight of ammonium chloride, suspend in 100 to 150 ml. of water in a 250-ml. flask, and pass ammonia gas through until the whole is dissolved.

Bromine Solution for Ethylene. Add bromine to a 10 per cent solution of potassium bromide until solution which does not attack clean mercury is obtained.

N.B.—It is essential to wash gas sample with potassium hydroxide solution after bromine has been used and before measurement.

Fuming Sulphuric Acid for Ethylene. Add sulphur trioxide to sulphuric acid until a strongly fuming acid is obtained.

Strong Solution of Silver Chloride in Ammonium Hydroxide for Acetylene. This reagent does not absorb ethylene.

Absorption Order. In analysing a gaseous mixture such as coal gas the absorptions must be prepared in the following order :

[1] Harden, *J. Sci. Inst.*, 1931, **8**, 332.

(1) Carbon dioxide with potassium hydroxide—absorption rapid.

(2) Oxygen with pyrogallol.

(3) Olefines with bromine water. All olefines are rapidly absorbed by this reagent; propylene is absorbed by 87 per cent sulphuric acid in 10 minutes, while ethylene is scarcely attacked, provided it is not present in excess. Similarly, the higher olefines are absorbed by 70 per cent sulphuric acid while propylene and ethylene remain.

(4) Carbon monoxide with ammoniacal cuprous chloride. It is essential to shake the gas with the reagent for 10 minutes and then to use a fresh portion of the reagent for a second washing. Ammonia is then removed from the gas with dilute sulphuric acid.

The gas is then exploded with oxygen and electrolytic gas. Each of the absorptions must be repeated until the volume of the gas ceases to diminish or does so only very slightly. If other constituents have to be determined the necessary absorbents are applied in the proper order, i.e. after all other constituents which could be absorbed by the reagent employed have been removed.

Combustion Analysis. Combustion is used for the estimation of unabsorbed gases. Hydrogen may be determined by explosion with oxygen in an explosion pipette; a known volume of oxygen is used and the excess absorbed after the explosion. When other combustible gases are present, as, for example, in a mixture of methane and hydrogen, a more elaborate process must be employed. A known fraction of the mixed gases is passed into the burette and from there into an explosion pipette. A volume of air or oxygen largely in excess of that sufficient to burn the gas is measured and passed into the pipette; a spark from an induction coil is passed across platinum terminals in the pipette, the gas being maintained under a reduced pressure. The residual gas, containing carbon dioxide, oxygen and nitrogen, is transferred to the burette and accurately measured. The carbon dioxide and excess oxygen are measured by absorption in the ordinary way. The volume of carbon dioxide produced is equal to the volume of methane originally present, and that of hydrogen may be calculated from the remaining data. Other mixtures of combustible gases can be determined in the same way. It is of advantage to add an equal volume of the gas obtained by the electrolysis of water to the mixture to be fired, as this ensures complete combustion, even when the original mixture is outside the explosive limits.

Device for Slow Combustion. A method of effecting the combustion of gases is to confine the sample in a vessel containing a platinum wire which is heated electrically, and add oxygen or air in a slow stream until a slight excess of oxygen has been added, and the whole of the combustible gas burnt.

In order for the process to take place without risk of explosions occurring, due to momentary high concentrations of oxygen, a fine control on the rate of oxygen inflow is necessary. It is also necessary to prevent loss of gas by back-diffusion into the oxygen supply.

In the design of Ambler,[1] the oxygen inflow is kept under close observation and control by bubbling through the side capillary A. This also eliminates all possibility of back-diffusion (Fig. 32 (I*)).

[1] *J. Sci. Inst.*, 1931, **8**, 18; *Analyst*, 1930, **55**, 436.

· The platinum coil consists of about 10 cm. of wire of 0·125 mm. diameter wound in a 2 mm. helix, and joined to wires of 0·5 mm. diameter, which are fused through the side limbs BB. The latter are made of tubing of 5 mm. bore, and are about 3 cm. in length. In the event of a break in the wire, it can be removed without destruction of the apparatus, by cutting the limbs BB near the ends, and replaced by fusing in again.

Where the composition of the gas is such that it can be exploded without oxidation of nitrogen, the explosion method may be preferred on the grounds of speed. The apparatus is found to be sufficiently strong to stand explosions
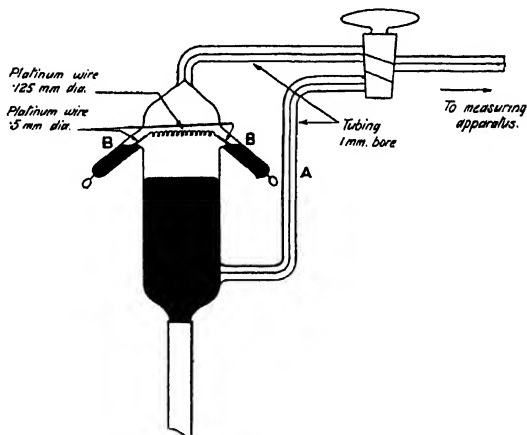
FIG. 32 (I*)

of gas mixtures containing up to 20 per cent of hydrogen, the highest quantity that can be accurately so determined.

The vessel can also be used for the absorption of gases in liquid reagents ; the absorption process may be assisted by bubbling the gas through the reagent. At the end of the process, gas is transferred back to the measuring apparatus with the tap in the position shown in diagram, until the reagent just passes through the tap ; the tap is then reversed and gas driven from the connexions by means of mercury through the capillary A. This eliminates the necessity for a special mercury reservoir for the purpose.

Drying of Gases. For the drying of gases various chemicals (e.g. calcium chloride, soda lime, sulphuric acid or phosphorus pentoxide) may be employed and a desiccating agent which will not react with the gas must also be selected. For general use calcium chloride is employed, but it is not very efficient and some moisture will still be retained by the gas. Dittmar and Henderson found that air dried by calcium chloride still retained 0·001 gram of moisture per litre of air. Air dried by sulphuric acid has been found by Dibbitts still to retain a trace of moisture (0·002 milligram of moisture per 100 litres of air). Drying by phosphorus pentoxide, especially with repeated circulation through the desiccating agent and allowing the gas to stand in contact with the phosphorus pentoxide, is the most efficient method of drying. By this method of intensive drying the fraction of water molecules can be reduced as low as 10^{-10}.

Adsorption of Gases (see chapter on Practical Methods in Colloid Chemistry). The adsorption of gases by silica gel and other similar materials may be studied by two methods, namely (a) *the static method* and (b) *the dynamic method*. In the first method the gel is contained in a small vessel which is highly evacuated at 300° and then placed in a thermostat at any desired temperature and a known volume of gas introduced. When equilibrium is obtained the pressure is observed and the amount of gas introduced recorded. This operation is repeated with the introduction of more and more gas.

In the dynamic method, the gel is placed in a U-tube (placed in a thermostat) and a known mixture of air and the gas under test passed over it. At first the gas is completely removed from the mixture with air, but after a time a small amount of it appears in the outcoming gas stream. It then appreciably increases, and after a short time the issuing gas is of similar composition to the entering gas. This is the saturation point of this mixture at a definite temperature.

FIG. 33 (I*)

The apparatus required for the examination of adsorption of gases by solids (e.g. silica gel, &c.) is simple (for the preparation of silica gel, see *Ind. Eng. Chem.*, 1926, *18*, 386). It consists essentially of a method of measuring the volume of gas or vapour before and after passing through the gel. It is also necessary to have a means of mixing air with the gas in fixed proportions. For the latter purpose an ordinary gas meter may be employed or the flow meter shown above. The apparatus used by McGavack and Patrick [1] for this study of the adsorption of sulphur dioxide by silicic acid is shown in Fig. 33 (I*). In general outline it is similar to that used by Homfray. The essential parts are the gas container A, the gas burette B, the adsorption bulb C, and the manometer D. These parts are all sealed together and mounted inside a constant temperature bath. This bath is a completely water-jacketed air-bath, with gas burners and carbon lamps. It is controlled by relays and a sensitive toluene mercury regulator. This bath has also been used in a study of osmotic pressure at high temperatures. The gas container is controlled by a sensitive valve and is dried by calcium chloride and phosphorus pentoxide. The burette (B) to contain the gas is connected by a U-joint to another U-tube of the same bore which serves as an open manometer. The gas burette is connected by glass tubing of narrow bore to a three-way stopcock which in turn leads to an expansion bulb. This serves as a precaution against too hasty introduction of the gas. The adsorption container C is connected to the expansion bulb by glass tubing, and the ground-glass connecting joint is protected by a mercury seal. The volume of the bulb and the
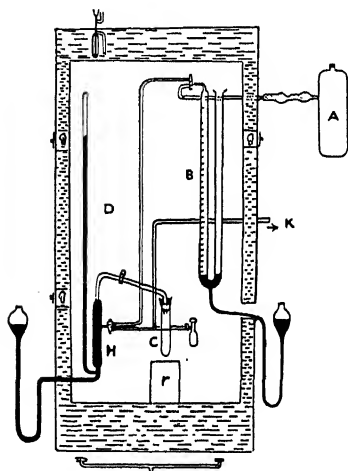
[1] *J. Amer. Chem. Soc.*, 1920, *42*, 946.

connecting tube is determined initially. In all the work a vacuum is maintained by using, in series, a rotary oil-pump and a Gaede high vacuum pump. A MacLeod gauge is attached at K to determine when evacuation is complete. The gel is weighed directly into the adsorption bulb which is then attached to the apparatus. The electric furnace (r), previously calibrated, is put in position for heating. Evacuation is then commenced. When complete, the adsorption bulb is allowed to fall to the temperature desired and the first introduction of gas made and the equilibrium pressure determined. More gas is then introduced and the pressure again determined. This is continued until atmospheric pressure is reached.

Adsorption of Gases by Cocoanut Charcoal. As an example of this type the adsorption of ammonia at different temperatures may be quoted :

Temperature	Vols. (ml.) of ammonia gas adsorbed per volume of carbon
0 .	. 175
20 .	. 150
30 .	. 135
40 .	. 114
50 .	. 95
60 .	. 88
70 .	. 82
130 .	. 20

Micro-Gas Analysis. The methods employed in micro-gas analysis may be classified under the headings of ' volumetric methods ' and physical methods. Volumetric methods have again been subdivided [1] under the headings (1) dry gas, variable volume method; (2) moist gas, variable volume method; (3) the diver method, and (4) the mica-plate method. The physical methods which adopt themselves to micro-analysis are (1) the spectroscopic method, (2) the thermal conductivity method, and (3) the dielectric constant method. In a paper by Hartridge [2] a general description of all these are given and this original should be consulted. Many references are given to the literature.[3] In the supplementary volume of Physico-Chemical Methods a section on *Micro-Gas Analysis* will be included.

[1] Hartridge, *J. Sci. Inst.*, 1939, *16*, 317.   [2] *Ibid.*
[3] See section on Micro-Gas Analysis in Farkas and Melville, *Experimental Methods in Gas Reactions*, MacMillan, 1939 (pp. 174–201).

SECTION 4: LIQUEFACTION OF GASES

The very large volume of material included in this subject makes even its elementary treatment difficult in this section. Davy and Faraday used a bent tube closed at both ends (Fig. 34 (I*)); the gas was generated in one limb and the other limb was cooled in a freezing mixture; practically all the commoner gases, with the exception of hydrogen, nitrogen, oxygen, carbonic acid, nitric oxide, and methane, were found to liquefy in the cooled limb. In 1877 Pictet employed a continuous cooling apparatus to produce a very low temperature and was able to liquefy oxygen. The method consisted in liquefying carbon dioxide by cooling it in liquid sulphur dioxide; the evaporation of the liquid carbon dioxide was used to cool the tube containing the oxygen under pressure; the latter was liquefied at the low temperature. Cailletet accomplished the same end by compressing the cold gas in a thick-walled capillary tube and suddenly releasing the pressure; a mist of liquid oxygen appeared in the tube.

FIG. 34 (I*)
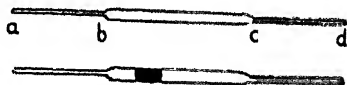
FIG. 35 (I*)

The work of Andrews on carbon dioxide shed a new light on the problem of liquefaction. It showed that a gas could not be liquefied, no matter what pressure was employed, unless the temperature was lower than a certain value, the critical temperature. This temperature is different for each gas. Andrews' experiments were carried out with tubes such as shown (Fig. 35 (I*)). The portion ab is capillary tubing; bc was 2·7 mm. in diameter and cd smaller. The capillary tubes were carefully calibrated. The volumes of the apparatus from a point on ab to two marks were also known. The tube was then filled with gas and the end a sealed. It was then manipulated so that the gas was confined in the upper portion of the tube by a plug of mercury. The tube was attached to one limb of a long U-tube containing mercury, and the pressures exerted by the gas when the mercury surface reached the selected marks were determined. From these readings the volume of the gas is calculated. The tube, enclosed in a water-jacket, was then placed in a compression chamber and readings of pressure and volume taken; a similar tube containing air, for which Boyle's Law was assumed to be correct, was used as a manometer. Readings were taken at a variety of temperatures, and curves were obtained such as

38

shown (Fig. 36 (I*)). The existence of a critical temperature is evident from the curves.

Critical Temperature and Critical Pressure. The temperature 31·1° in this case is called the critical temperature for carbon dioxide, and at no higher temperature, no matter what pressure is applied, can the gas be liquefied. The corresponding pressure at the critical temperature is called the critical pressure and the corresponding volume the critical volume.

Determination of the Critical Temperature and Critical Pressure. A quantity of liquid is heated in a sealed tube and the temperature at which the line of separation between the liquid and vapour disappears gives the critical point. The 'Boyla tube' shown in Fig. 37 (I *) can be used for this observation. The tube XY, contain-

FIG. 36 (I *)

ing, e.g., ether, is suspended horizontally between two vertical planes of glass and is electrically heated by Z. In case of explosion the plates of glass prevent splinters spreading. After some time the meniscus becomes less defined and on disappearing a mist forms in the tube. The temperature
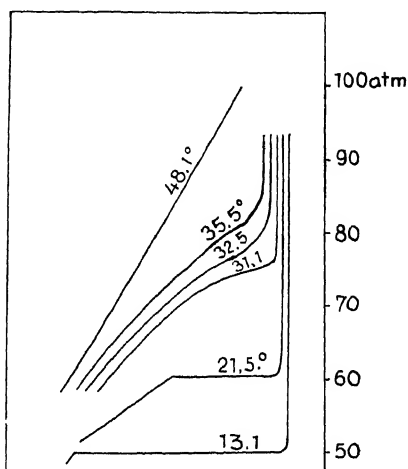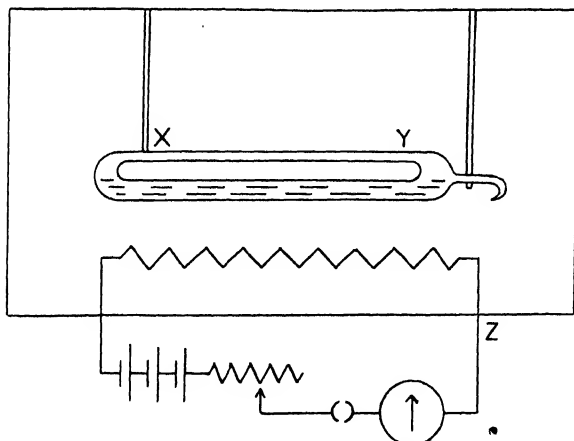

FIG. 37 (I *)

at this stage is the critical temperature. On slightly heating further the tube becomes clear and then contains only gas. On cooling, the reverse process occurs. This only gives the critical temperature.

This method is not accurate if the substance contains traces of impurities which delay the setting up of equilibrium. In more accurate determina-

tions the tube is connected to a manometer and the liquid is agitated during the heating. The temperature at which a very slight decrease in pressure causes the meniscus to temporarily appear until the temperature of the substance re-establishes itself is the critical temperature. Cardoso [1] in case of other than permanent gases uses the disappearance of the critical opalescence as the measure of the critical temperature.
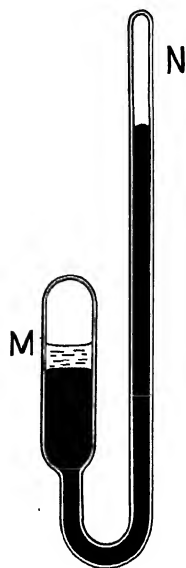
For the critical pressure the apparatus of Gaignard de la Tour, or a modification of it, can be employed. This consists of a hard glass tube (Fig. 38 (I *)) containing a liquid above the mercury at M. In the other limb of the tube at N air is enclosed. On heating, the liquid above M behaves similarly to that in the above experiment in the Boyla tube. The pressure can be calculated utilizing Boyle's Law.

In the modern methods for critical temperature using the manometer the critical pressures can be obtained at the same time as the critical temperatures. Hacksfull and Mathieu [2] heated the sealed tube (containing phosgene) in a cylindrical block of aluminium heated electrically.

For an excellent review of the literature relating to the critical constant of various gases, see Pickering.[3]
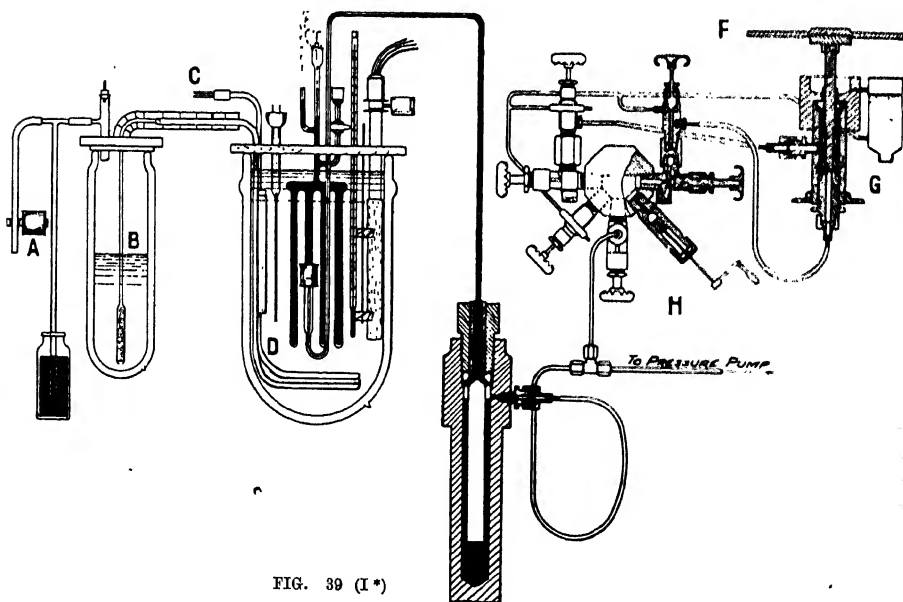
FIG. 38 (I *)

The critical constants and vapour pressure at high pressures of a number of gaseous fluorides have been investigated utilizing a very accurate form

FIG. 39 (I *)

[1] *J. Chem. Phys.*, 1910, *10*, 491.   [2] *Bull. Soc. Chem.*, 1919, *26*, 482.
[3] *Sci. Papers Bur. Standards*, 1926, 541.

of apparatus by Booth and Swinehart.[1] Their apparatus is shown in Fig. 39 (I *). The Cailletet tube was used which allowed for complete immersion of the sample. The magnetic stirrer E in the Cailletet tube (Fig. 40 (I *)) was a glass-enclosed iron wire with a small glass rod attached which held the wire in the top part of the tube and allowed clear vision of the sample. The thermostat used ($\pm$ 0·01°) gave constant temperature within very narrow limits for at least 20 minutes and at the same time had flexibility in adjustment. It consisted of a 3·7 Dewar jar having a mercury-filled thermoregular which actuated the magnetic pinch clamp A, causing the pressure developed by the boiling in B to force the liquid air into the cooling core D. A dead-weight manometer was employed. G is the dead-weight gauge consisting of a differential piston.[2] The two surfaces of the pisto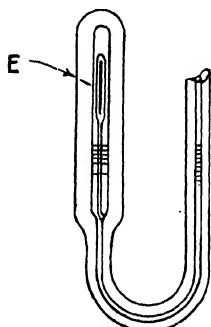n in the manometer were shown to be straight, &c., within very small dimensions. The diameters at 21° were measured using an optical lever micrometer against Johansen standard gauges and found to agree within $\pm$ 0·00002 inch.

The method used by Booth and Swinehart [3] for adjustment to critical conditions required more time than the older methods,[4] but was more accurate. When the critical point was approached the pressure gauge was shut off and the volume of the sample regulated by the threaded plunger until with rising temperature the meniscus disappeared without movement from the centre of the tube. The temperature was noted on the thermometer. Then with the gauge corrected, the temperature was adjusted to a slightly lower temperature. After equilibrium was set up (10–15 min.), the temperature was raised slightly and equilibrium again established. This process was repeated until the highest temperature at which the two phases could be seen was found. If the critical point is approached in this way, no opalescence is observed and the flat meniscus will be seen to broaden out at a definite temperature becoming little more than a striation which completely disappears if the stirrer is moved and does not re-form. This is the critical point.

Detail of Cailletet Tube
FIG. 40 (I *)

Note on the Separation of Mixtures of Gases. The liquefaction of gases with subsequent fractionation is often a convenient method of separating gas mixtures. Ramsay and Travers used this method for the separation of the rare gases of the atmosphere. The separation of the constituents of natural petroleum gases has been made by a similar method. An improved apparatus for such work and for many problems of gas separation has been described by Shepherd and Porter.[5] Péntcheff [6] estimated neon in natural gas by removing all the other gases except neon and helium by charcoal at the temperature of liquid air fractionation, and determining the density of the resulting mixture.

[1] *J. Amer. Chem. Soc.*, 1935, *57*, 1337.
[2] Cf. Meyers and Jessup, *Bur. Stand. J. Res.*, 1931, *6*, 1061.
[3] Loc. cit.   [4] For references, see Pickering, loc. cit.
[5] *Ind. and Eng. Chem.*, 1923, *15*, 1143.   [6] *Compt. rend.*, 1929, *189*, 323.

Liquid Air.   Liquid air is now produced in large quantities by application of a self-cooling arrangement.   The air is compressed to a small volume and then suddenly allowed to expand by means of a valve ;   work is done against the molecular forces of the gas and the latter is cooled and eventually liquefied.   The process is made a continuous one in the Linde and Hampson processes.

Dewar Flask.   The manipulation of liquefied gases has been simplified by the introduction of the Dewar vacuum flask ; the usual forms are shown in Fig. 41 (I *).   The space between the walls is thoroughly evacuated, so heat transference across the gap is minimized. Liquid air evaporates only very slowly from one of these vessels.
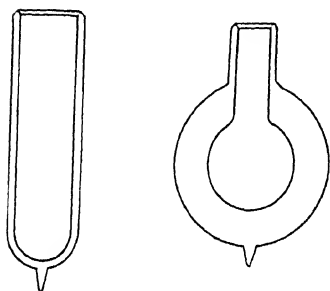
The separation of the rare gases of the atmosphere from atmospheric nitrogen and from one another was accomplished by this method.

It has been shown by Meisser [1] that in the best containers available (with specially good vacuum and silvered surfaces to prevent radiation losses), hydrogen is rapidly lost, especially with large containers.   In a 6-litre vessel evaporation accounted for the loss of 15 grams (200 ml.) of hydrogen per hour.   In a special design worked out by Kapitza and
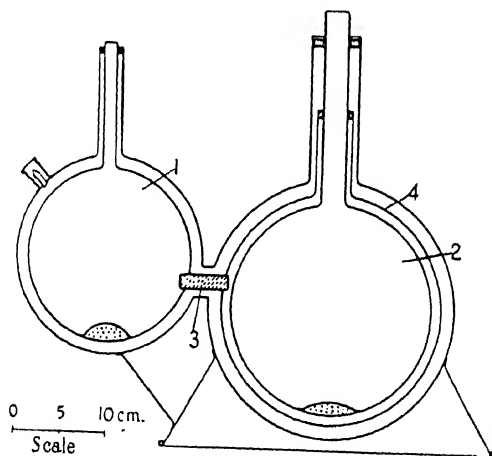
FIG. 41 (I *)

FIG. 41A (I *)

Cockcroft [2] an improved form has been secured.   The container consists of a twin-flask (Fig. 41A (I *)).   The first flask (2 litres) contains liquid air and the second flask liquid hydrogen (5 litres).   The inside of flask 1 is connected by means of a copper rod 3 to a copper shield 4 which surrounds the container of flask 2.   The liquid air cools the shield 4 by thermal con-

[1] *Z. Inst. Kunde*, 1930, *50*, 121,   [2] *Nature*, 1932, *129*, 255,

ductivity, and the radiation losses from the liquid hydrogen are considerably reduced. The evaporation of hydrogen is 2·5 grams per hour. The consumption of liquid air is about 1·7 litres per day.

Fractionation. Fractional distillation at low temperatures of the condensate obtained on cooling of the gases can be carried out in apparatus very similar to that employed in the ordinary fractionation of liquids, except that the fractionation column must be specially cooled.

The fractionating column is kept cool by circulating brine of − 15° to − 17°. A condensation method involving freezing in liquid air and subsequent measurement of vapour pressures with a Pirani gauge has also been described by which very small quantities of gases can be analysed.[1]

In special cases the gas mixtures may be separated by other methods, e.g. by absorption of one or more of the constituents in some solvent or in some substance with which a compound is formed and fixed.

Purification of Gases by the Method of Stock.[2] The method was originally employed in connexion with the purification of boron hydride.

Briefly, the method is to treat magnesium boride (impure) with hydrochloric acid in a slow stream of inert gas (hydrogen) and to collect the gases evolved in a U-tube in liquid air. The mixture is then pumped away slowly, so that only the most volatile fractions are removed (hydrogen and silicon hydride). The temperature is gradually raised and ultimately a definite fraction of constant vapour pressure (at a given temperature) is evolved. This is collected in a second U-tube in liquid air. When the pressure starts falling again, the evolved vapour is again pumped away, and so on. They are then left with several crude fractions which are fractionally distilled at low temperature and pressure again, the fractions being collected this time in small bulbs.

The apparatus thus consists essentially of a good pump (or pumps), and a long train of U-tubes connected with by-passes and glass taps, the U-tubes being so arranged that they can be surrounded by cooling baths in Dewar flasks. Wherever necessary in the apparatus, there are manometers.

The method may be used to purify any gas which liquefies at a convenient low temperature and pressure.

Mulders and Scheffer[3] have given a method of analysing mixtures of ethane, methane, and hydrogen, by cooling in liquid air, followed by subsequent fractionation and burning the fractions separately over copper oxide. A similar method was used by Walker and Shukla[4] for methane and ethane. The combination of this method with the palladium absorption method for hydrogen has been described by the same authors,[5] using 5 to 10 ml. of the gaseous mixture. The apparatus employed is shown in Fig. 42 (I *). It consists of a Töpler pump connected by a three-way stopcock A to (i), the U-tube which can be cooled by immersion in a vacuum vessel containing liquid air, for removal of the ethane, and to (ii) the palladium bulbs C for hydrogen removal. The tubes B and C are connected

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[1] *Proc. Roy. Soc.*, 1921, *33*, 287.

[2] Alfred Stock, Ernst Kuss, and Otto Briess. Borwasserstoffe, *Ber.*, 1914, *47*, 3115.

[3] *Rev. trav. Chim.*, 1930, *49*, 1057.   [4] *Trans. Far. Soc.*, 1931, *27*, 35.

[5] *J. Chem. Soc.*, 1931, 308.

respectively to the mercury traps D and D', the transferring pipette
and G', and to the bent capillary tubes F and F' dipping into merc
troughs.   The hydrogen absorption apparatus is similar to that emplo
by Grice and Payman,[1] but improved by the introduction of the merc
trap and by the use of the steam-jacket.   After being measured in
Bone and Wheeler burette the gas sample is transferred through F to
The apparatus is evacuated and the U-tube immersed in liquid air
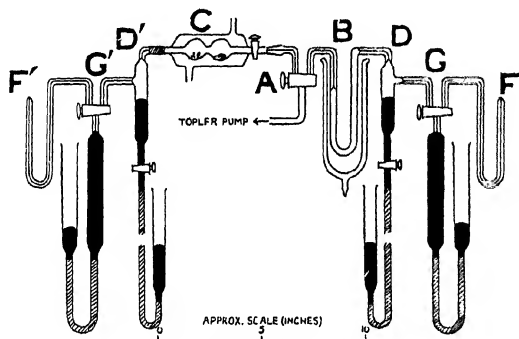
FIG. 42 (I *)

raising the Dewar vessel.   A is then closed and the sample transferred to B.
After 5 minutes, connexion is again made to the pump and the hydrogen
and methane removed.   The palladium tube is then evacuated and the
steam passed through the jacket to tube C.   The sample is then introduced
to C and allowed to remain in contact with the palladium at 100° for
20 minutes.   The steam is replaced by cold water and when the tube C
is cold the residual methane can be pumped off and weighed.   A complete
analysis can be carried out in 1½ hours.

[1] *Fuel*, 1924, *3*, 236.

SECTION 5: SEPARATION OF GASES BY SOLUTION

A description is here given of a typical fractional solution method investigated for the separation and collection of gases.[1]

The separation of one gas from another by treatment with a liquid by which one is almost completely absorbed, and the other practically not at all, is a frequent operation both technically and in the laboratory. Such absorptions, however, are generally chemical, and proceed almost independently of the changing partial pressures of the gases which are being treated. On the other hand, the use of liquids in which one gas is much more soluble without chemical action than the other is infrequent, principally because the law of partial pressures renders it impossible completely to separate two gases in this way. Its chief application at present is the separation by washing with water of carbon dioxide from the hydrogen and carbon monoxide in water-gas with a view to the ultimate utilization of the hydrogen.[2]

The graphical method which is here used can be applied to other instances of fractional solution and to other fractionation processes, e.g. fractional evaporation. For simplification the particular case of hydrogen and carbon dioxide as obtained in the n-butyl alcohol-acetone [3] fermentation process is taken for consideration.

In this process 100 lb. of maize (containing 65 per cent of starch) gives approximately 39 lb. of carbon dioxide (as gas), 0·9 of carbon dioxide (in solution), and 1·1 lb. of hydrogen. The carbon dioxide formed is equivalent to about 350 cubic feet at 20° and 760 mm., while the hydrogen is equivalent to slightly over 200 cubic feet under the same conditions.

In the small experimental plant shown in Fig. 43 (I *), a mixture of gases was passed up two towers in series where it met a descending stream of water. Carbon dioxide dissolved to a much greater extent than hydrogen, and the gas leaving the second tower had the composition H_2 95 per cent, CO_2 5 per cent, as compared with H_2 40 per cent, CO_2 60 per cent for the original entering gas. To economize water the gas in the towers was washed at a total pressure of 11 atm. as at increased pressures greater volumes of gas are dissolved. But, as shown by the solubility curve in Fig. 44 (I *), carbon dioxide (as the pressure increases) dissolves less readily than would be expected from Henry's law. Accordingly, it is more economical to work at as low a pressure as possible consistent with the volume of gas under treatment; 11 atmospheres (161·7 lb. per square inch) was found most suitable for the material available. A low temperature increases the

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[1] Blair, Wheeler and Reilly, *J. Soc. Chem. Ind.*, 1922, XLII, 22, pp. 235 T–240 T. The related diagrams are from this article.

[2] Reilly and Blair, U.S.A. patent 21475/1925.

[3] Reilly, Hickenbottom, Henley, Thayen, *Bio. Chem. J.*, 1920, XIV, 229.

45

40% H₂
60% CO₂

40% H₂
60% CO₂

95% H₂
5% CO₂

85% H₂
15% CO₂

L

H

R

B 2

P.G.

P.G.

P.G.

P.G.

P

W

TO SPRAY

P.2.

P.1

FROM SUMP

P.G. L TO WASTE

TO SPRAY

W

C   Gas compressor   H   H.P. relief valve
I   Crude gas inlet   L   L.P. relief valve
O   Purified gas outlet   P   Perforated plates
R   Recovered gas return   W   Water seals
P₁P₂ Water pumps

FIG. 43 (I*)

Cubic feet of CO₂, measured at 1 atm. and 15°, dissolved by 1 cubic foot of water at 15°.

Total pressure in lb. per square inch.
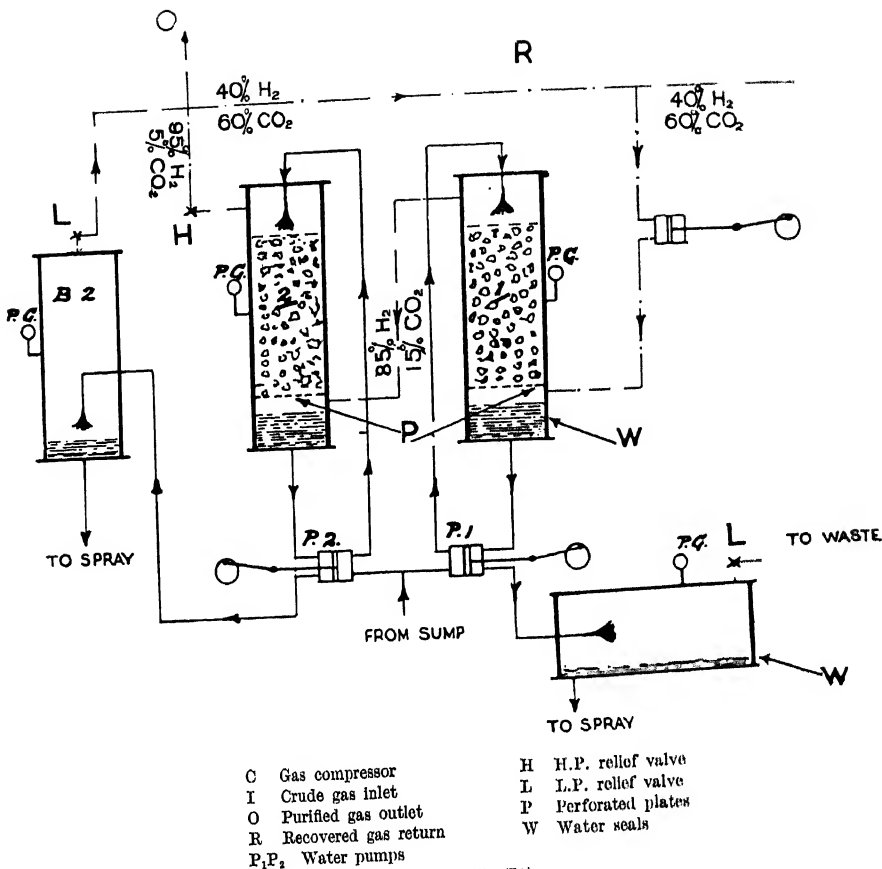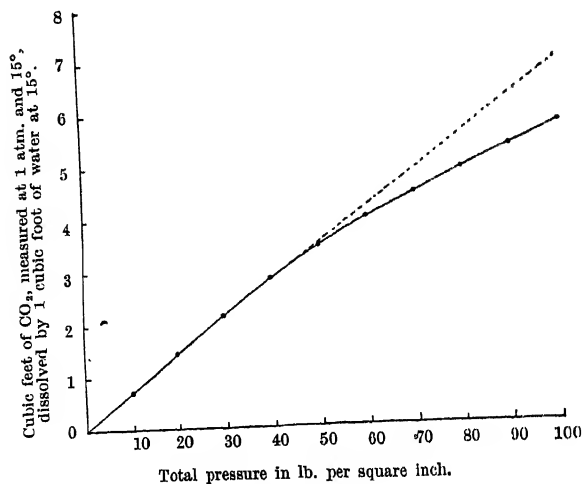
FIG. 44 (I *)

46

solubility of the gas ; for the purposes of this investigation the temperature employed was approximately 15°.

The solubility of hydrogen in water under various pressures at 15° very closely follows Henry's law, and at ordinary pressure and temperature has about 0·02 of the corresponding solubility of carbon dioxide.

The effect of washing at a constant pressure 100 cubic feet, measured at a given temperature and pressure, of acetone fermentation gas may now be considered. The gas is assumed to pass up a tower down which the water flows, and the tower is taken to be of such a size that with the rate of gas passage used there is time for the entering gas to come into equilibrium with the water flowing away. Also the 100 cubic feet of gas and the corresponding quantity of water are taken to be very small compared with the total quantity of gas and water passing through the tower.

Let S_1 be the solubility, measured in cubic feet at the temperature (15°) and pressure of the entering gas, of hydrogen at 15° at its partial pressure in the entering gas, and let S_2 be the solubility, measured in cubic feet and at the same temperature and pressure as S_1, of carbon dioxide at 15° at its partial pressure in the entering gas. Let a cubic feet be the quantity of water used to treat 100 cubic feet of the entering gas measured at its own temperature and pressure, and finally let the percentage of hydrogen in the gas entering the tower be b and the percentage of hydrogen in the gas leaving the tower be b_1. Then the quantity of hydrogen leaving the tower corresponding to 100 cubic feet of entering gas is $b - S_1a$ and the quantity of carbon dioxide is $100 - b - S_2a$, so that

$$\frac{b - S_1a}{100 - b - S_2a} = \frac{b_1}{100 - b_1} \tag{i}$$

and $$ab_1(S_1 + S_2) - 100aS_1 - 100(b_1 - b) = 0 \tag{ii}$$

Hence, given S_1 and S_2, a can be calculated if b and b_1 be known, and vice versa. Also the volume of the exit gas is $100 - a (S_1 + S_2)$ cubic feet. In the same way the effect of washing $100 - a (S_1 + S_2)$ cubic feet of gas in a second tower can be determined.

The subject can now be developed by means of graphs. Fig. 45 (I *) shows a series of graphs giving the quantity of water required at 15° and 11 atm. total pressure to wash 100 cubic feet (measured at 15° and 1 atm.) of gases containing from 40 per cent of hydrogen upwards, so that the issuing gas may contain any given percentage of hydrogen up to 100 per cent. These graphs have been calculated from equation (i) making the assumptions given above ; it will be noted that allowance has been made for the varying solubilities of carbon dioxide above 35 lb. per square inch pressure, otherwise all the graphs would meet A B at a. It is obvious from Henry's law that the quantity of water required to wash in the manner described the less soluble constituent from 100 cubic feet of a mixture of two gases, the solubilities of which are constant, is independent of their proportions in the entering gas. This can be proved directly from equation (ii) ; if 100 be substituted for b_1, s_1b for S_1, and $s_2 (100 - b)$ for S_2, a will then be found to be independent of b. The condition can also be expressed in equation (i).

Curve C D is important since it represents the washing of the gas actually

to be dealt with in the first tower. The curves other than C D could be applied to the second tower, were it not that the quantity of gas entering the second tower is not 100 cubic feet. The quantity of gas leaving the first tower can, however, easily be determined from the quantity of water used ; the dotted line C F shows the quantity of gas left after the initial 100 cubic feet has been washed to any given percentage of hydrogen.

Percentage H, in washed gas
Curve C V F shows volume of gas absorbed in tower
FIG. 45 (I *)
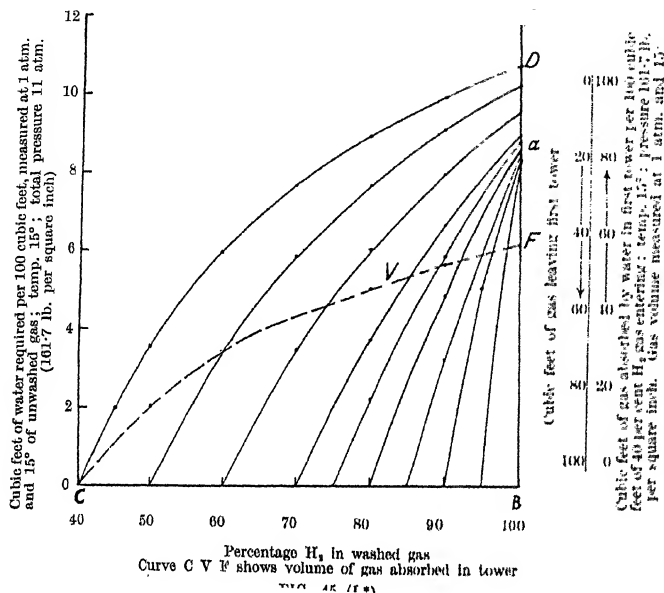
If now the curves in Fig. 46 (I *), other than C D, have their ordinates reduced to correspond with the quantity of gas at each percentage entering the second tower, we obtain a series of graphs C D, $C_1 D_1$, &c. (Fig. 46 (I *)), of which C D is the same as in Fig. 45 (I *), and applies to the first tower; the remaining graphs apply to the second tower. The quantity of water necessary to wash 100 cubic feet of a 40 per cent hydrogen gas to any given hydrogen percentage in the first tower, and to any other higher percentage in the second, can now be directly determined. Thus the water required to have a 70 per cent gas entering the second tower, and a 90 per cent hydrogen gas leaving it is represented by AB + EF = AG. Other points G_1, G_2, can be determined similarly, and a graph is obtained showing the quantity of water required to wash 100 cubic feet of a 40 per cent gas to 90 per cent in two towers, the abscissae representing the percentage of hydrogen in the gases between the two towers. The curves for a 70 per cent, a 90 per cent, a 100 per cent gas are also given.

The quantity of water required in the second tower to obtain any final gas with any intermediate gas can be obtained; for a 90 per cent hydrogen final gas and 70 per cent intermediate, an ordinate A P is erected equal to E F, and so on. The curves for 70 per cent, 90 per cent, 95 per cent and 100 per cent final gases are given.

Percentage H₂ in gas between towers

FIG. 46 (I*)

Percentage H₂ in gas between towers

FIG. 47 (I*)

49
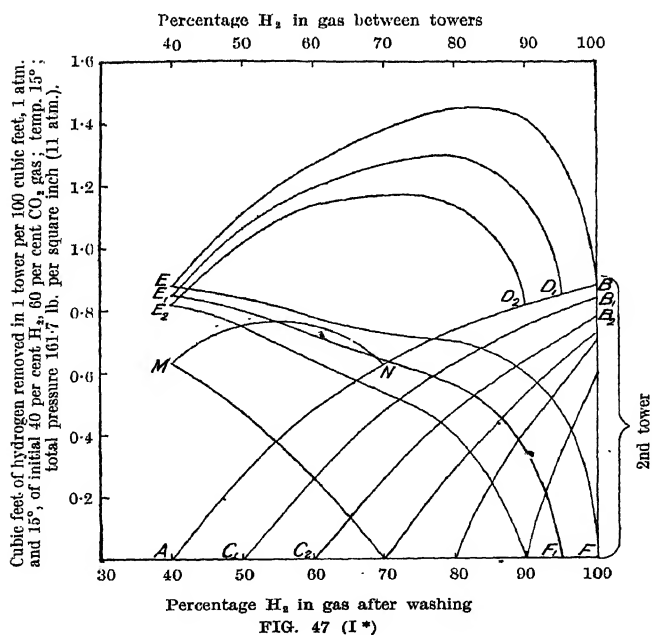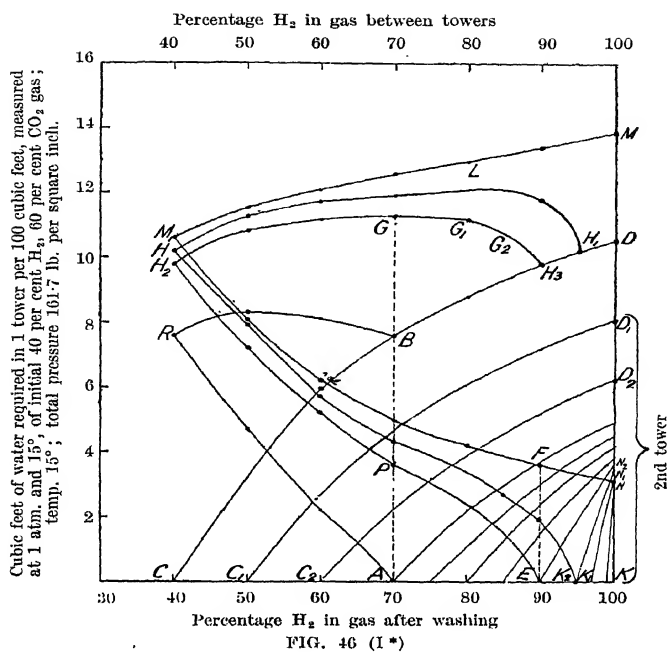
Here, again, the point N is not on the 100 per cent curve ; and the point K is a singular point to it.

The quantity of hydrogen removed by the water flowing from the towers is also of importance ; it is obtained by multiplying the quantity of water used by the solubility of hydrogen at the partial pressure at which water is in equilibrium with it.

Curve A B in Fig. 47 (I *) shows the quantity of hydrogen dissolved by the water flowing from the first tower. Curves C_1B_1, C_2B_2 show the quantity of hydrogen for 100 cubic feet of 40 per cent hydrogen gas entering the first tower, removed by the water in the second tower to obtain gases of compositions up to 100 per cent. Curves E B, $E_1 D_1$, &c., show the total quantity of hydrogen dissolved in washing the same initial gas to 100 per cent, 95 per cent, 90 per cent and 70 per cent hydrogen gases with varying intermediate gases between the towers ; curves E F, E_1F_1, &c., give the quantities of hydrogen dissolved in the second tower in washing to the various hydrogen percentages shown, the percentage of hydrogen in the gas between the towers being the abscissa. These curves are all obtained from the curves A B, C_1B_1, &c., in a manner similar to that described for curves H H_1, &c., and curves H K_2, &c., in Fig. 46 (I *).

The absorption of carbon dioxide in the manufacture of hydrogen is now a well-established process. In addition to water, many other absorbents are used in the absorption system. The Standard Oil Development Company and the Girdler Corporation in one process use a solution of diaminoisopropanol as absorbent. For references to other work on this problem, see Sherwood's book on *Absorption and Extraction* (McGraw-Hill, 1937).

SECTION 6: DENSITY OF VAPOURS

Determination of Density. The density of a gas may be defined as the mass per cubic centimetre of the gas under standard conditions. Owing to the fact, however, that the relative densities of gases approximate to half their relative molecular weights, it is found convenient to express the density relative to that of some standard gas. Hydrogen has not been found a convenient standard, so the gas selected is oxygen, whose density under standard conditions is taken as 16. The relative density of the gas is therefore the mass of any volume of the gas compared to the mass of the same volume of oxygen under standard conditions of temperature and pressure. The standard temperature is taken as the melting-point of pure ice, and pressure as one of 760 mm. of mercury at 0° at sea-level in latitude 45°.

The gas equation $pv = RT$ applies exactly only to the so-called 'ideal' or 'perfect' gas. Actual gases show deviations from the laws and the well-known equation of Van der Waals'

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

is an attempt to find an equation which will fit in better with the experimental results with real gases. The correction in the first term is for the attractions of the molecules on each other and that in the second for the actual volume of the molecules themselves. When v becomes very large, or, what is the same thing, the pressure and density become very small, these corrections become negligible, and at zero pressure the equation reduces to that for the ideal gas: for other pressures at constant temperature $p_1 v_1 / p_0 v_0$ is not equal to 1. (See Vol. I, p. 80.)

In the same way Avogadro's hypothesis is only exactly correct at zero pressure. If therefore we wish to make use of this hypothesis to calculate the relative molecular weight of a gas, the densities used must be those which the gas would have at zero pressure reduced by the ideal gas equation to N.T.P.: these are called limiting densities by D. Berthelot.

With sufficient accuracy we may assume that at constant temperature the density alters linearly with the pressure when this lies between 0 and 1 atm.

Then
$$D_0 = D(1 - Ap)$$

where D_0 is the density of the gas in the ideal state, D the density determined at the pressure p, and A is the compressibility constant for the gas. In this equation both densities are the weights in gm. of one litre of the gas at 0° and one atmosphere pressure.

The molecular weight of the gas compared with oxygen = 32

is then
$$M = \frac{D_0 \times 32}{1 \cdot 4279}$$

51

where 1·4279 is the density of oxygen at N.T.P. in the ideal state. Some values of A are hydrogen, — 0·064 ; oxygen, 0·076 ; carbon dioxide, 0·674 ; sulphur dioxide, 2·358.

If the densities at N.T.P. are calculated from the weights of gas filling a volume v at $0°$ and at pressures p_1 and p_2 and these densities are called D_1 and D_2

$$D_0 = D_1(1 - Ap_1) = D_2(1 - Ap_2)$$

so that A can be calculated and then the limiting density D_0 and from that the molecular weight.

Direct Method. This method consists in determining the weight of a gas enclosed in a globe of known capacity under definite conditions of temperature and pressure. The weight of the globe filled with water at a known temperature is also found, so that the density of the gas with reference to water is known. The globe consists of a thin glass bulb sealed to a capillary stopcock. To eliminate small errors due to changes in pressure, temperature, &c., during the weighing, a similar bulb is used as a counterpoise. The dimensions of the globes may vary with the volume of gas at hand. Ramsay and Travers used globes of 160 ml. capacity in the case of argon and other gases, of 33 ml. in the case of helium and neon, and of 7 ml. for xenon. The globe must be cleaned and dried thoroughly and the stopcock seen to work freely. It is then exhausted by a pump and weighed. It is next filled with boiled water and placed in a constant-temperature bath for some time, with the stopcock open. When the water has assumed the temperature of the bath the stopcock is closed and the flask carefully dried, the excess water being removed from the capillary. The flask is again weighed. When the weight of gas is later obtained it may be compared with that of the water at the known temperature. The density globe is then carefully dried and exhausted ; it is again weighed. The dry gas is allowed to enter the globe by means of a gas burette ; after standing for some time the temperature and pressure of the gas in the bulb is obtained and the latter once more weighed.

The absolute weight of a litre of the gas can be calculated from the formula

$$W = \frac{w}{v} \times \frac{(273 + t)}{273} \times \frac{760}{P} \times 1,000$$

where w = weight of the gas contained in the globe at temperature $t°$
    under a pressure P
  v = volume of the globe at temperature $t°$

The weight of a litre of oxygen may be similarly determined. Taking oxygen as 16, the relative density of the gas is obtained by proportion.

A correction must be made for the fact, pointed out by Lord Rayleigh, that the globe loses buoyancy when it contracts on exhaustion. The contraction may be determined and corrected for.

The general method described is that used by Ramsay and Travers in their researches on the rare atmospheric gases. The other principal workers in this field of recent years are Leduc, Rayleigh, and Morley.

Morley's investigations were on the densities of oxygen and hydrogen ; precautions were taken to eliminate all possible error. The globes used were of capacity of 8 to 20 litres. The weights were determined by the

method of double weighing. Both mercurial and air thermometers were used in the temperature measurement. A number of different methods were used to measure the pressure. The gases were usually brought to the temperature of melting ice before a measurement.

Rayleigh weighed the gases in a globe of known volume, into which they were introduced at the temperature of melting ice and under a pressure fixed by means of a special manometer beforehand. The counterpoise method was adopted and the correction for loss of buoyancy made.

Leduc's investigations were carried out with globes of about 25 litres. His results are lower than those of other observers.

The $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium may be studied by the direct method of density determination. The globe is filled with nitrogen tetroxide at the laboratory temperature and the density determined. The globe is then placed in a thermostat at a definite higher temperature and the tap opened for a moment to adjust the pressure. The density is then determined at this temperature. This operation is repeated at various temperatures up to 100°. The nature of the equilibrium can be studied from the density data.

Vapour Density. The determination of density has a very important application in the case of substances which can be obtained in the gaseous state; the molecular weight of such substances may be obtained by determining the volume of vapour under standard conditions, produced from a known weight of the substance. The three best known methods for such determinations are those of Dumas, Hofmann, and Victor Meyer.

Method of Dumas. This is essentially the same as that already described for gaseous densities. The bulb is of 50 ml. to 100 ml. capacity, and is shaped as shown (Fig. 48 (I *)). The volume of the bulb is found by weighing it full of air and then filled with boiled water; the first weighing, minus the weight of air, obtained from tables, gives the weight of the empty globe. Knowing the density of water at the temperature of the second weighing, the volume of the globe is calculated.

Several grams of the liquid substance are then placed in the bulb, which is immersed in a constant-temperature bath about 20° higher than the boiling-point of the substance;

FIG. 48 (I *)

the latter boils, driving out all the air in the globe. When the vapour ceases to leave the mouth of the globe the latter is sealed off near the end in the blowpipe; the globe is then again weighed, giving the weight of vapour enclosed at the known temperature and pressure. The density is easily calculated and reduced to standard conditions.

Method of Hofmann. The method is originally that of Gay-Lussac, though the name of Hofmann is usually associated with it. The procedure is the reverse of that of Dumas. A known weight of substance is vaporized and the volume it occupies at a known temperature and pressure
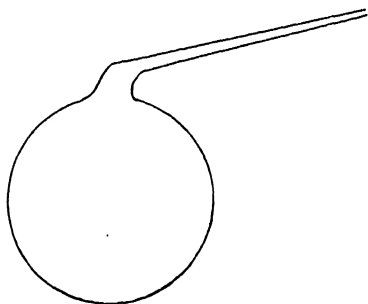
is measured. The apparatus employed is shown in Fig. 49 (I *). An inner barometer tube about a metre long and 10 to 12 mm. in bore is filled with mercury (taking the usual precautions against the presence of air or moisture) and inverted in a mercury trough ; a Torricellian vacuum is, of course, formed at the top of the tube. The tube is graduated in cubic centimetres and millimetres. This inner tube is jacketed by a wider tube ; the boiling vapour of a suitable liquid is passed in at the top and passes out through the lower side-tube. The liquid under experiment is weighed in a special bottle containing about 0·1 ml. and introduced above the mercury. The liquid is vaporized and depresses the mercury in the barometer tube. The height of the mercury column is measured ; the
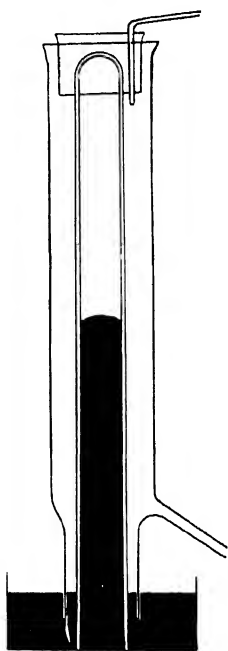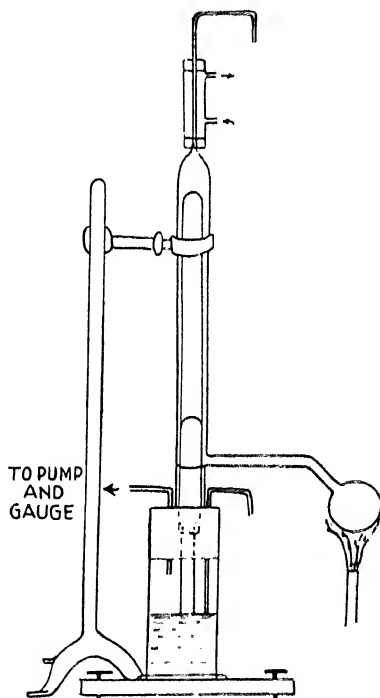
FIG. 49 (I *)   FIG. 50 (I *)

vapour is then under a pressure equal to that of the atmosphere minus the height of the mercury column. Its temperature is that of the surrounding vapour and its volume is directly measured. The latter is then reduced to standard conditions and the density calculated.

A correction must be introduced for the temperature of the mercury column ; the height measured must be multiplied by the factor for the density of mercury at $t°$, and the barometric height dealt with similarly before the difference is obtained. If the temperature used is high a correction for the vapour pressure of mercury must be made ; in practice, however, high temperatures are not usually necessary, as the vapour is under diminished pressure.

Hofmann's apparatus has been modified by Ramsay and Young, so

that the external pressure could be altered and the observations taken at different temperatures and pressures with the same quantity of substance. The apparatus is shown in Fig. 50 (I *). In place of the ordinary shallow trough a cylindrical gas-jar is employed. An india-rubber stopper, perforated with one large central hole and two small holes near the sides, closes this. The vapour-density tube passes through the central hole and its lower end is immersed in mercury. One side-tube is connected with an exhaust and compression pump and two gauges so that the pressure on the mercury can be regulated and measured. The other tube is fitted with a stopcock and reaches nearly to the bottom of the cylindrical jar. The vapour jacket is connected to a pump and gauge, so that the boiling-point of the liquid in the outside bulb can be altered. Fluctuations of pressure are avoided by interposing a glass globe of about 10 litres capacity between the jacketing tube and the gauge.

Victor Meyer's Method. In principle the method is much like that of Hofmann; the weight of the original substance is fixed and its volume as vapour is measured. In Victor Meyer's method, however, the gas measured is an equal volume of air displaced by the vapour of the substance. The method is very convenient and is much used where extreme accuracy is not required.

The apparatus usually consists of a long-necked cylindrical bulb of about 100 ml. capacity, furnished with a side-tube at the top (Fig. 51 (I *)). The bulb is surrounded by a wider tube, bulb-shaped at the end. The side-tube on the inner tube leads to a gas-measuring tube. In most cases this consists of a graduated eudiometer tube standing in a deep-water reservoir. Sometimes a gas burette with an adjustable reservoir containing water is used as shown.

The liquid is contained in a Hofmann bottle and weighed. Liquid with a boiling-point 20° to 30° above that of the experimental liquid is placed in the outer bulb and boiled. The air in the inner bulb expands and is driven over through the side-tube; when all air has ceased to come over, the eudiometer tube is filled with water and inverted over the end of the delivery tube. The stopper of the bottle is then loosened, the cork of the inner tube momentarily removed, and the bottle dropped in. The cork is immediately replaced. The bottom of the inner bulb must be protected from fracture by means of a layer of sand or asbestos. The liquid in the bottle is immediately vaporized and air bubbles are driven over into the graduated tube. When air has ceased to be driven over, the delivery tube is removed and
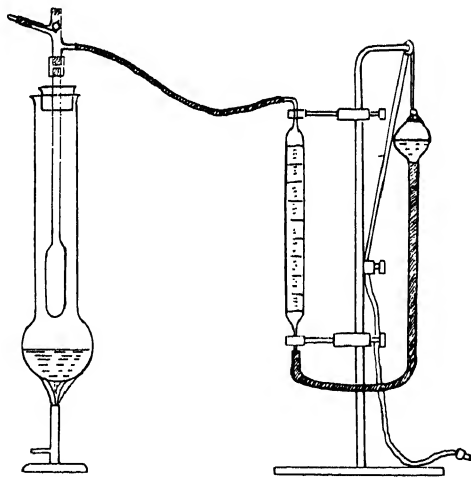
the air allowed to stand some time to attain the temperature of the water. It is then depressed in the reservoir until the water-level is the same inside and outside the tube and the reading taken. If the collection has not taken place in a deep reservoir the tube must be transferred to such before measuring the volume. The temperature of the water and the atmospheric pressure are read at the same time. The use of the collecting apparatus shown in Fig. 51 (I *) will be obvious.

Pressure Correction. Before calculating the vapour density it is well to discuss the determining factors in the experiment as described. When the vaporizing occurs a quantity of air equal to the increase in volume is forced out from the upper part of the inner tube and collected over water. The assumption is that the increase in volume is completely due to the vapour ; it is probably more correct to deduct the volume of the bottle from the final volume, but the correction is a negligible one under the conditions of the experiment. The displaced air changes during the experiment from the temperature of the tube to that of the atmosphere ; it is assumed that the vapour would undergo the same change in volume, since the experiment is based on the gas laws. When the final measurement is made the air in the eudiometer is saturated with water vapour. If the air in the upper portion of the inner tube is saturated with water vapour before the displacement, no correction should be introduced to the atmospheric pressure. If, on the other hand, the air is originally perfectly dry, the vapour pressure of water at atmospheric pressure should be deducted from the observed barometric height. Finally, if the air originally is partly saturated, as is probably the case, the correction is that fraction of the aqueous vapour pressure which the air originally lacked. Since the apparatus is originally filled with room air and this air is finally brought back to room temperature, it is probable that the correction should include the difference between the aqueous pressure in the room and the saturated aqueous pressure at room temperature. The room aqueous pressure is usually over 50 per cent. The corrected barometric reading is therefore

$$\mathrm{B} - \frac{100 - x}{100}p$$

where B = observed barometric height

p = saturation vapour pressure of water at room temperature

x = percentage saturation of air of room

If V is the volume of air measured at temperature t, and corrected pressure P, then

$$\text{Vapour density} = \frac{W.760(273 + t)}{V.P.\ 273} \text{ grams per millilitre}$$

Modified Method. The original apparatus has been improved in some details. A very necessary improvement in the method of introducing the bottle is described by MacInnes and Kreiling [1] (Fig. 52 (I *)). A glass tube fits closely through the stopper of the vaporization tube and a brass rod slides in this ; a gas-tight rubber tubing joint prevents leakage. The brass rod and tube dip nearly to the end of the inner bulb and the rod carries the experimental liquid enclosed in a thick-walled bulb at its end. The

[1] J. Amer. Chem. Soc., 1917, 39, 2350.

bulb ends in a sealed capillary bent into an inverted **V** and hangs on a hook fixed on the end of the rod. The liquid in the bulb may attain the temperature of the jacket before being allowed to vaporize. To allow the latter, the brass rod is pulled up and the capillary broken against the glass tube. Vaporization occurs instantly and very little mixing with air occurs.

In the same communication these workers describe an improved form of the Victor Meyer apparatus. Uniform heating along a tube 50 cm. long is difficult to produce by boiling vapour in the tube ; ordinarily the air at the bottom of the vaporization tube will be warmer than that at the top. The expansion of the substance at the bottom displaces, therefore, the colder air into the measuring tube. This colder air will have a larger volume in the measuring tube than the air immediately displaced by the vaporized substance would have if brought down to the same temperature.
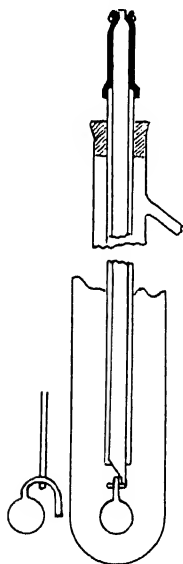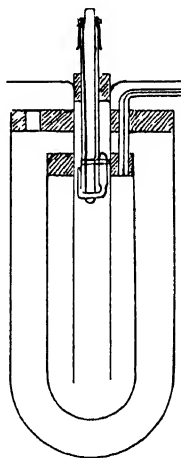
FIG. 52 (I *)   FIG. 53 (I *)

To eliminate this difficulty the tube was modified as shown in Fig. 53 (I *). The vaporization vessel, which is 25 cm. long and 5 cm. wide, carries a rubber stopper, through which passes a capillary delivery tube, and another tube of 15 mm. bore and about 28 cm. long. In this a breaking apparatus of the above type is placed. The whole is enclosed in the boiling-tube which is closed by a split stopper. A sheet of asbestos, supported by a rubber band, deflects the vapour away from the top of the breaking apparatus. The substance to be vaporized may be fastened to the breaking apparatus by a rubber band. A gas burette is found more satisfactory in collecting the gas with this apparatus. It is also necessary to have the vapour jacket 80° above the boiling-point of the substance under investigation.

The Lumsden Modification. In the Victor Meyer method the increase in volume is measured. In this modified method the increase in pressure

is measured.   The apparatus (Fig. 54 (I *)) consists of a bulb A (100 ml.) surrounded by a heating jacket B and attached to a manometer C.   A weighed quantity of substance is dropped into the bulb, there converted into vapour, and the pressure measured before diffusion takes place. The jacket B may contain liquids for low boiling-point work.   For higher temperature, two concentric tubes (FF) may be screwed to an iron sole and between the tubes tin or other metal in small grains may be employed and the condenser H eliminated.   A substance of known molecular weight is used to calibrate the apparatus and the pressure (p) equivalent to that for a gram-molecule calculated.   The molecular weight (M) is given by the equation $M = x\dfrac{p}{p_1}$, where x = the weight of vapour, and p_1 the noted pressure.

The apparatus may also be modified for use at reduced pressure and it may also be filled with inert gas instead of air.

Density of a Gas from its Percentage Composition.   In addition to the well-known methods described above for the determination of gas densities, other methods are sometimes employed, especially when a lower order of accuracy only is required.   If the composition of the gas mixture is known its specific gravity can be calculated by multiplying the percentage content of the simple gases by their specific gravity and dividing by 100 according to the formula :

FIG. 54 (I *)

$$(0\cdot0695\ H_2 + 0\cdot9671\ CO + 1\cdot1877\ H_2S + 0\cdot5543\ CH_4$$
$$+ 1\cdot0\ C_nH_{2n} + 2\cdot8\ C_nH_{2n-6} + 1\cdot5184\ CO_2$$
$$+ 1\cdot1055\ O_2 + 0\cdot9673\ N_2)\tfrac{1}{100}$$

The Specific Thermal Conductivity and its Relation to Gas Density.   This constant (K) is defined as the number of calories required to enter unit area of plane A in order that the temperature of planes A and B may remain constant at $T - I°$ and $T°$ respectively where the planes are unit distance apart.   It depends upon the density of the gas.   With decreased density there is increased conductivity.

The thermal conductivity of a number of gases are recorded in the following table :

Helium	33·9
Hydrogen	39·7
Air	5·68
Ammonia	4·58
Carbon monoxide	4·99
Carbon dioxide	3·07
Methane	6·47
Nitrogen	5·24
Nitrous oxide	3·50
Oxygen	5·63

The method is especially applicable for technical control analysis using self-indicating apparatus ; e.g. such a method is used in the estimation of sulphur dioxide in flue gases.

The earliest method of measuring the thermal conductivity of gas was that of Schleiermacher. He utilized the fact that a platinum wire stretched along the axis of a glass tube immersed in a water-bath assumes a temperature when heated by a constant electrical current which depends upon the nature of the gas surrounding the wire.

From the measure of the thermal conductivity of a gas mixture a continuous analysis of a gas mixture is possible. The method employed is
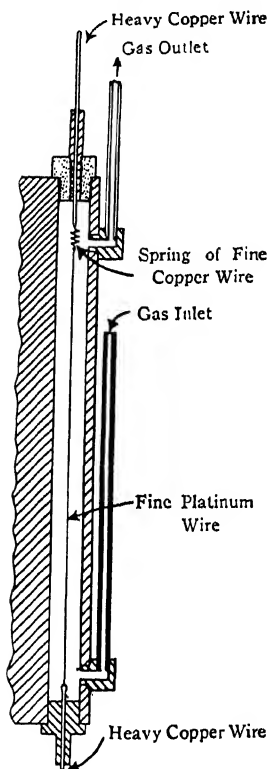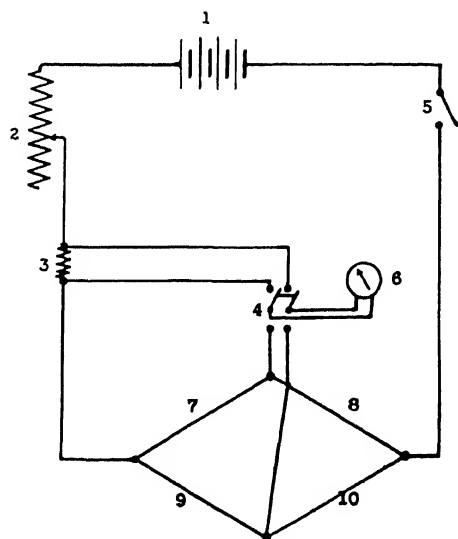

FIG. 55 (I *)

1, Battery ; 2, Rheostat ; 3, Drop coil (shunt) ; 4, Double Knife, double throw switch ; 5, Switch ; 6, Indicator ; 7–10, Wires exposed to gas mixture ; 8–9, Wires exposed to comparison.

FIG. 56 (I *)

outlined below, but original papers should also be consulted for details of manipulation.

Fig. 55 (I *) shows the apparatus in which the gas is contained. There is a fine platinum wire passing through the tube. This unit will form one arm of a Wheatstone bridge. The calibration depends on the comparisons with gases of known composition. The arrangement of Koepsel is shown in Fig. 56 (I *). In the Bureau of Standards methods a balanced bridge arrangement is employed. Two wires constitute two arms of the Wheatstone bridge (see Fig. 57 (I *)) and a Kohlrausch slide wire together with extension resistances form the other two arms. A galvanometer indicates the balance point.
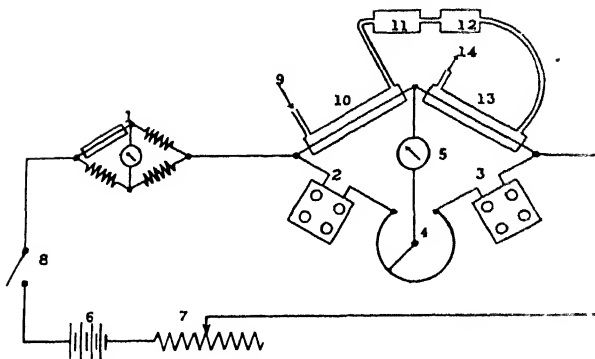
FIG. 57 (1*)

1, Current adjustment bridge; 2 3, Four-dial resistance boxes; 4, Slide wire bridge; 5, Galvanometer; 6, Battery; 7, Rheostat; 8, Switch; 9, Entrance for gas mixture; 10, 13, Thermal conductivity cells; 11, Carbon dioxide absorber; 12, Drying tube; 14, Exit for residual gas.

Velocity of Sound in Gases in connection with Density Determination. Geberth[1] has shown that the density of a gas can be deduced from a study of the velocity of sound in the gas. His apparatus is capable of estimating hydrogen within 0·1 per cent. The gas is placed in a closed cylinder and the length of the cylinder is adjusted until resonance is obtained with a vibrating diaphragm which is electrically maintained. In Griffith's apparatus[2] a somewhat similar method is employed and supersonic vibrations are used.

The Effusion Method of Density Determination. The density of a gas may be quickly determined by this method, which in one or other form is employed in most technical gas analyses. It depends on the principle first indicated by Bunsen that equal volumes of two gases issue from a small opening at rates proportional to the square roots of the densities, P_1 or P_2 of the gases respectively,

$$\frac{P_1}{P_2} = \frac{t^2_1}{t^2_2}.$$

The comparison is generally made taking air as the standard.

The following table gives the *rate of effusion* of some common gases:

Gas	Density p	$\frac{1}{\sqrt{p}}$	Rate of Effusion	Diffusion Vol.
Hydrogen . .	0·0693	3·8	3·613	3·83
Methane . .	0·5590	1·3375	1·322	1·34
Nitrogen . .	0·9713	1·0147	1·016	1·01
Oxygen . .	1·1056	0·9510	0·950	0·98
Carbon dioxide	1·5290	0·8087	0·821	0·81
Nitrous oxide	1·5270	0·8092	0·834	0·82

Various types of works apparatus for the determination of the effusion constant can be purchased from instrument makers and with these are

[1] *J. Ind. and Eng. Chem.*, 1923, *15*, 1277.
[2] *Proc. Phys. Soc.*, 1927, *39*, 30.

given details of practical working. A simple form of apparatus for the determination of the density of gas is shown in Fig. 58 (I *). The method depends on the determination of the velocity of effusion of a gas. When a gas flows through a small opening (less than 0·01 mm. diameter) the velocity of flow obeys the same law as for liquids, i.e. $V = \sqrt{2gh}$, where $h =$ the depth of orifice below the surface. Air at 0° and 760 mm. pressure issuing through an aperture into a vacuum has a velocity of approximately $\sqrt{2 \times 981 \times 790,000}$ cm. per second, the value of h being the height of a homogeneous atmosphere. With different gases V is proportional to the square root of their densities. In a vessel A containing mercury a glass tube is plunged. To the upper end of the tube is cemented a piece of platinum foil C in which a fine hole is made. Closing this with the finger, the tube is filled with mercury and the gas, whose effusion rate is required, is allowed to displace the mercury. A glass rod F drawn out with a long stem is introduced and floats in the mercury in the tube B. On this stem are two marks, the

FIG. 58 (I *)

upper mark is brought level with the mercury in the outer vessel by allowing a little of the enclosed gas to escape. Now removing the finger from C the time is noted which elapses until the lower mark is level with the mercury. To test the density of a specimen of gas (e.g. coal gas), the gas may be allowed to stream from a constant-pressure gas-holder through a small gas-holder connected with the tube B by flexible tubing. The quantity of gas that escapes in a given time being thus measured.
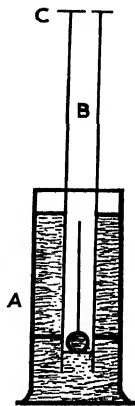
A reference will be made to one apparatus suitable for accurate work. In the apparatus of Hofsäss [1] the gas reservoir consists of a wide cylindrical tube connected above and below with narrow tubes provided with efficient taps. The tube of the lower end communicates with an open manometer tube containing a suitable liquid, while the tube at the upper end serves for the introduction of gas into the apparatus and communicates with a side-tube with a perforated diaphragm, which can be shut off from the reservoir by a tap. During an experiment this tap is open and the time required for the fall of the manometer liquid over the distance fixed by two marks on the manometer tube is measured by means of a stop-watch.

The effusion method may be employed for the determination of the molecular weights of saturated vapours in the glass effusion apparatus of Eyring.[2] The apparatus (shown in Fig. 59 (I *)) has a minute opening at N made through a thin glass bulb which is sealed into the apparatus. After evacuating the system, F and K are closed and a weighed bottle containing mercury and the liquid under examination (approximately 5 ml. each) is placed at A and mercury drawn up until it reaches the stopcock B, which is then closed. The apparatus is again evacuated, being then closed. The weighing bottle is then lowered slightly and B opened until sufficient liquid is drawn into the apparatus. The weighing bottle is raised, mercury again

[1] *Chem. Zeit.*, 1913, *11*, 1353 ; *J.C.S. Abstracts*, 1913, *11*, 1026.
[2] *J. Amer. Chem. Soc.*, 1928, *50*, 2398.

being drawn up until any liquid in the neighbourhood of the stopcock B has been displaced. After introducing the liquid, the stopcock F was turned and at the same time a stop-watch was started and the time noted for the mercury in the manometer to rise a marked distance. The same operations are repeated with air (as standard, the mean molecular weight being taken as 28·9). The following data were obtained by Eyring with
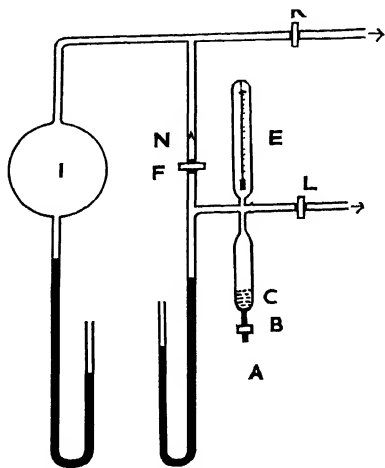

FIG. 59 (I *)

isopropyl alcohol : time for air 140 seconds. Time for isopropyl alcohol 202 seconds. Molecular weight of isopropyl alcohol $\left(\dfrac{202}{140}\right)^2 \times 28·9 = 60$.

The whole determination takes less than $\frac{1}{2}$ hour and no weighing is required. The method can be applied to gases and all vapours with vapour pressures greater than that of water. The range can be extended to lower vapour pressures by making more accurate pressure measurements or by raising the temperature.

SECTION 7 : SPECIFIC HEATS OF GASES

Importance of Determination. The ratio of the specific heat of a gas at constant pressure to the specific heat at constant volume is of importance in the determination of the atomicity of a gas, i.e. the number of atoms in one molecule. This ratio, denoted by γ, can be shown theoretically to be 1·66 for monatomic gases and to be less than 1·66 for polyatomic gases. Experimentally it has been shown that γ is 1·66 for gases such as mercury, helium, argon, &c., so that these gases are monatomic. Gases such as hydrogen, oxygen, nitrogen, which are supposed for other reasons to be diatomic, are found to give values close to 1·41 for γ, while more complex gases such as carbon dioxide give still lower values.

The Ratio of Specific Heats of a Gas. The ratio could be found by determining the two specific heats separately ; but this is not a simple matter, and because there exist two methods by which the ratio can be determined directly, this is the procedure usually adopted. In Clément and Desormes' method a large vessel A [Fig. 60 (I *)], furnished with a tap B having a very wide bore, and a water manometer aa' to indicate the pressure of the gas, was used. The air was partially exhausted so that the water rose to a. After sufficient time had been allowed for temperature equilibrium to be set up, the reading of a was taken and the tap B was opened for a moment and closed. When B is opened the pressure in A rises to atmospheric : this compression is regarded as adiabatic and is accompanied by a rise of temperature ; the liquid in the manometer of course falls to b when the tap is opened. When the gas falls to the temperature of its surroundings, its pressure falls and the liquid rises to a'. Then
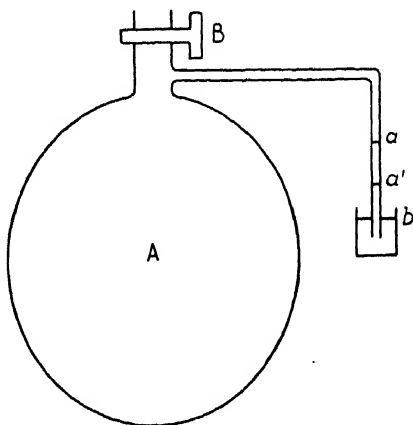

FIG. 60 (I *)

$$\frac{ab}{aa'} = \frac{\text{adiabatic elasticity}}{\text{isothermic elasticity}}$$

Modified Apparatus. Fig. 61 (I *) shows the details of the neck of another form of apparatus for carrying out the experiment. Here the large flask A is inverted and contained in a wooden box in which it is well packed with some heat-insulating material. The neck is short and wide and projects from the bottom of the box : it is closed with a rubber stopper carry-

63

ing the manometer C, which contains some liquid such as α-bromo naphthalene (D = 1·481 at 25°), the inlet tube D which passes to the top of the flask and the wide tube having a tap with a large bore B. A light gas may
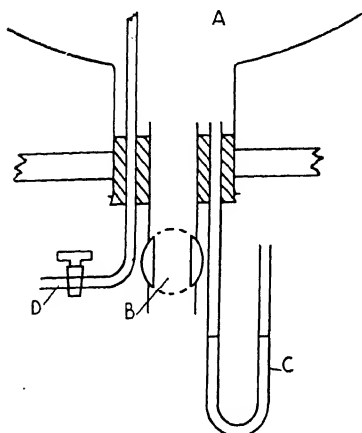

FIG. 61 (I *)

be passed in through D, displacing the air through B; a heavy gas can be passed in the opposite direction. The passage of the dry gas is continued until all the air has been displaced. The outlet tap is then closed until the pressure has risen to about 12 cm. of the manometer liquid : the inlet tap is next closed and the apparatus allowed to stand for 15 minutes. The manometer reading is taken and the tap B is opened for 2 seconds and then closed. After 10 minutes the manometer reading is again taken ; all the data for the calculation of the ratio of the two specific heats have been obtained.

In the improved apparatus of Partington [1] an expansion vessel of 130 litres capacity is employed and thin leads are employed to the resistance thermometer made of very fine platinum wire (bolometer) with compensating leads. An Einthoven string galvanometer capable of recording temperatures in 0·01 second is employed. An outline of the apparatus is shown in Fig. 62 (I *). The vessel A has an expansion valve C which is worked by the aid of a
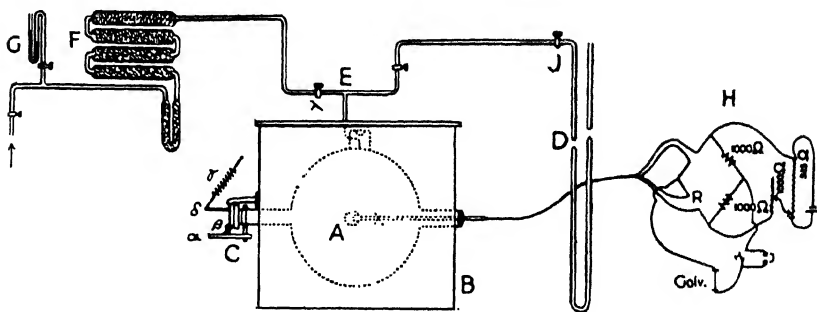
FIG. 62 (I *)

spring. A is connected to the manometer D (containing sulphuric acid), the mercury manometer G and the drying tube F. The dry pure air enters A, which is agitated in a water ball. The bolometer wire (Fig. 63 (I *)) B is connected to one arm of a Wheatstone bridge. The bolometer is also shown separately in Fig. 63 (I *). A thermometer (not shown) records very accurately the temperature of the bath. The resistance

[1] *Proc. Roy. Soc.*, 1921, A, *100*, 27, and cf. Saha and Srivastava, *Treatise on Heat*, The Indian Press, 1935, p. 92.

in one arm of the Wheatstone bridge was arbitrarily reduced to give a deflection on the galvanometer. The initial pressure of the gas was arranged so that immediately after expansion this deflection was reduced to zero. After expansion ice was continuously added to the ball to keep the temperature constant and similar to that just before the expansion. In practice the diameter of the aperture in the valve could be varied by
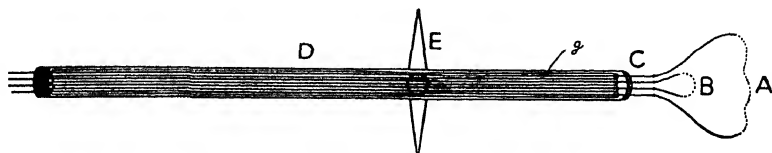

FIG. 63 (I *)

inserting diaphragms of brass plate which were screened tightly against the rim of the neck and caulked with a little red lead and linseed oil. The method is not suitable for use at high temperature owing to the difficulty of applying a cooling correction.

The Second Method (originally due to Kundt). It enables a comparison of the velocity of sound in two gases to be made, and if one of these be a gas such as air, for which the velocity is known, that in the other gas can be calculated.

The velocity (v) of sound in a gas is given by the expression

$$v = \sqrt{\frac{\gamma p}{d}}$$

where γ is the ratio of the two specific heats, p is the pressure in dynes per square centimetre, and d is the density of the gas.

Apparatus. To compare the velocities, a wide glass tube about $1\frac{1}{2}$ metres long and fitted with side-tubes and taps for the introduction of the gas is employed (Fig. 64 (I *)). Through a cork A in one end of the tube passes a short glass rod having a disc of cork E, which fits the tube fairly tightly. Through the other end B, passes a glass rod C, clamped at its middle point G and having a disc of cork or cardboard at F, which
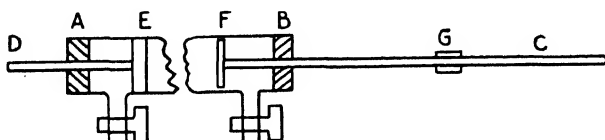
FIG. 64 (I *)

just clears the sides of the tube. The stopper B was made of layers of sheet rubber tied round with silk, since it was found that if a cork was used this gave too rigid a connexion and its vibrations disturbed the vibration of the gas in the tube. When the rod C is stroked longitudinally with a damp cloth it vibrates longitudinally and emits a high note : the longitudinal vibrations are transmitted by the disc F to the air column in the tube and

if the distance between E and F is an exact number of half wave-lengths the gas will be set into stationary vibration. The point E will be near a node, while F will be near a loop ; it will not be exactly there because although the vibrations of F excite the air, the amplitude of the vibration in the latter soon exceeds that of F. The position of the nodes is shown by placing a layer of some light powder such as lycopodium in the tube : this will be found to accumulate in heaps at the nodes. The piston E is moved until the resounding air gives out a clear loud note and the powder will then be found to collect into very well defined heaps. The average distance between the nodal heaps gives the half wave-length $\frac{\lambda}{2}$ and we thus have the relation $V_1 = n \times \lambda$, where n is the frequency of the note. If now a second gas be placed in the tube, n remains the same, but V_2 and λ_2 will be different, the relation $V_2 = n \times \lambda_2$ holding.

We then have

$$\frac{V_1}{V_2} = \frac{n\lambda_1}{n\lambda_2} = \frac{\lambda_1}{\lambda_2}$$

This gives the ratio of the velocities, and if the second gas be air we know V_2 and so can get V_1. The relation $V_1 = \sqrt{\frac{\gamma_1 p_1}{d_1}}$ then enables us to calculate γ_1. In carrying out an experiment the tube AB is first very thoroughly dried and a layer of dried lycopodium is placed inside and evenly distributed by shaking ; the dried gas is then led in through the side-tubes to displace the air, and when this has been done the taps are closed. The rod C is set into vibration by striking with a damp cloth and the piston E moved until the maximum of resonance is obtained. The distance between the second and sixth, third and seventh nodes, and so on, is measured with dividers and so the average of four half wave-lengths is obtained, from which λ is calculated. A similar experiment is then carried out with dried air in the apparatus.

Modified Apparatus. This apparatus is shown diagrammatically in Fig. 65 (I *). It consists of a double wave-tube apparatus, with one
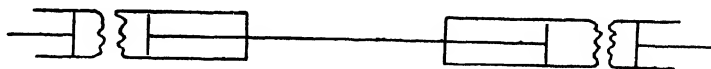
FIG. 65 (I *)

sounding rod supported by rubber caps in the ends of the two tubes at points one-quarter of its length from each end. When stroked in the middle it vibrates with a frequency corresponding to its first overtone. Pistons are provided for the adjustment to exact resonance, and each tube contains one of the two gases to be compared. The apparatus has the advantages that the dust figures correspond to a note of exactly the same pitch and that no temperature corrections are required.

The originally Kundt method has been modernized by Saha [1] and more

[1] *Ind. J. Phys.*, 1931, **6**, 445.

recently by Felsing and Jessen [1] especially in regard to the production of sound. A telephone receiver at one end of the gas tube is corrected to a variable high frequency vacuum tube oscillator which serves as a source of sound. The receiver was placed inside a machined brass fitting, a special graphite packing being employed to secure a gas-tight joint between the glass tube and the coupling enclosing the telephone receiver. The determinations are carried in a thermostat. The procedure of a determination involves the evacuation of the apparatus to pressures less than 0·001 mm., filling with pure air, setting the oscillator at a definite constant frequency, and determining the nodal distances. After evacuating as before, the gas under test after drying is admitted and with the identical oscillator frequency the nodal distances again determined. The value of the thermal capacity ratio γ is calculated from the usual formula :

$$\gamma = 1{\cdot}403(M/29{\cdot}0)(l^2{}_2/l^2{}_1)$$

where 1·403 is the value of γ for air, 29·6 is the molal weight of air, M is the molecular weight of the gas or vapour being tested and l_1 and l_2 are the experimentally determined nodal distances for air and the test gas respectively. The term thermal capacity or *thermal capacitance* of a substance is defined by Ferguson [2] as the quantity of heat required to raise the temperature of unit mass of that substance through 1°. In this connexion Ferguson states that there is a distinction between thermal capacitance as above defined and specific heat defined as a ratio. That thermal capacitance should be ·expressed in calories per degree, or some equivalent unit, and that a name should be given to the unit of specific heat—if the ratio definition be retained—it is merely an accident of definition that the number which measures a specific heat is the same as the number which measures a thermal capacitance.

Direct Determination of Specific Heat. The specific heats of gases are low and the bringing of a small volume of gas into an enclosed space would cause only a very slight rise in the temperature of the calorimeter. It is therefore necessary to use a method in which a comparatively large volume of gas is passed through a flow meter, the gas is circulated through a heated coil and the increase in temperature of the gas measured. This is done with the aid of thin wires which act as resistance thermometers. The method of Scheel and Heuse,[3] using a closed system with continuous flow, has been much used. The gas may also be passed through a thermostat and then into a coil placed in a calorimeter at a higher temperature. This method has been used by McCollum for the determination of the specific heat of gaseous nitrogen tetroxide.[4] The apparatus is shown in Fig. 66 (I *). A thermostat is mounted over a second thermostat, which contains a calorimeter. The lower instrument was I°–3° warmer. The gas in passing through a glass coil A to the coil B tended to lower the temperature of the inner can of the calorimeter. This cooling effect was exactly counterbalanced by regulating the current through the heating coil I to maintain a zero reading on a recording instrument. It has been modified

[1] *J. Amer. Chem. Soc.*, 1933, *55*, 4420.   [2] *School World*, 1937, *18*, 347–51.
[3] *Ann. Phys.*, 1919, *59*, 86.   [4] *J. Amer. Chem. Soc.*, 1927, *49*, 28.

by Thayer and Stegman,[1] by Haas and Stegman,[2] and by Felsing and Jessen.[3] The apparatus used by the latter workers is shown in Fig. 67 (I *)

The calorimeter was made of pyrex glass. The heating unit was made of 300 cm. of double silk-covered manganin wire wound on a small glass
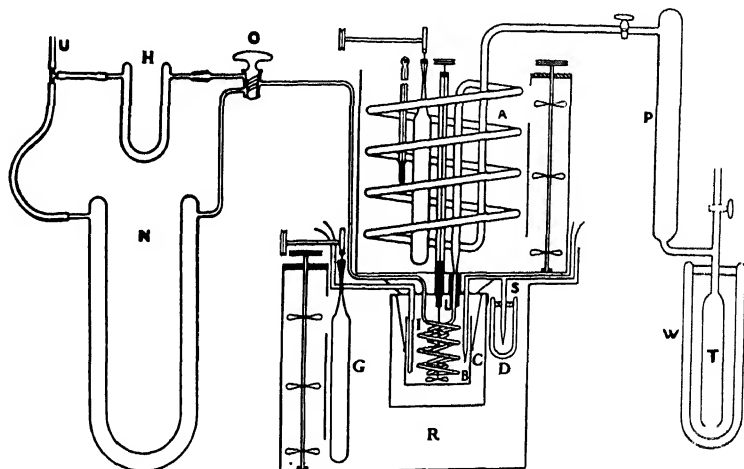

FIG. 66 (I *)

shellacked tube. The brass tube T was machined to fit the glass tube F of the calorimeter, placed inside, and attached by de Khotinsky cement. The copper tube E was closed at its lower end by means of a fine copper-wire gauze, soldered on. The space between the inner walls of this tube and the heater coil was packed with finely shredded copper B. All temperature measurements were made with a 15-junction copper nickel thermo-element according to the recommendations of La Mer and Robertson.[4]

Calibration of Apparatus. The apparatus was highly evacuated for 6 to 8 hours before filling with pure air. The specific heat of the gas was calculated by the relation:

$$\bar{c}_p(\text{watt-sec.}/g) = (E/M\Delta T)(1 - K/M^2)$$

where E is the energy input in watts, M is the mass of gas passing through the heater unit per second, ΔT the temperature rise, and K the heat lost constant of the calorimeter.

A modified constant flow method has been described by Blackett, Henry, and Rideal[5] which avoids the difficulty of measuring the temperature of the inflowing

FIG. 67 (I *)

and outflowing gases. For details of the theory of the method and experimental working of the apparatus the original should be consulted. The method is claimed to be accurate to about 1 per cent.
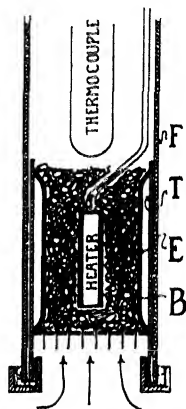
[1] J. Phys. Chem., 1931, 35, 1505.   [2] Ibid., 1932, 36, 2127.
[3] J. Amer. Chem. Soc., 1933, 55, 4418.   [4] J. Phys. Chem., 1931, 35, 1953.
[5] Proc. Roy. Soc., 1930, 126, 313; and Henry, ibid., 1931, 133, 492.

CHAPTER II *

SEPARATION PROCESSES INVOLVING VAPORIZATION

SECTION 1: DISTILLATION

DISTILLATION processes take advantage of the fact that the more volatile constituents of a mixture of components when partially vaporized occur in increased concentration in the vapour phase. By repeated distillations or by distillation through a fractionating column, separation of the components of a vaporizable mixture can, generally speaking, be effected.

'Flash' distillation involves vaporization of the mixture in an enclosure (entailing equilibrium between the vapour and liquid phases) until the desired amount of vaporization is completed. The vapours are then removed for condensation. This method of equilibrium vaporization may be conducted in a continuous manner as in the 'Pipe' stills used in the Petroleum industry.

For 'evaporative' (non-equilibrium) distillation, see later.

The usual laboratory apparatus for simpler distillation purposes, together with particular applications, are well known.

Electrical Heating. For some purposes it is convenient to employ an electrically heated coil of platinum wire as the source of heat. As recommended by Matthews and Richards, the vessel has the form shown in Fig. 1 (II *). This arrangement secures that the platinum wire is completely immersed, when the volume of liquid is very small. The platinum wire is about 40 cm. long, and of resistance 0·73 ohm. The ends of the platinum wire are sealed into two glass tubes, in which are stout copper leads. Connexion between the platinum and copper wires is effected by means of a little mercury. German-silver wire has been recommended in place of platinum wire. An electrically heated metal plate is a useful source of heat in some distillations. The amount of heat may be regulated by moving a piece of asbestos pasteboard over the surface of the heated plate, the flask being placed a little distance over the surface of the plate. In connexion with

FIG. 1 (II *)

distillation at constant volume, the use of an electrical hot plate and water-jacket to secure regular distillation is described later. (p. 115)
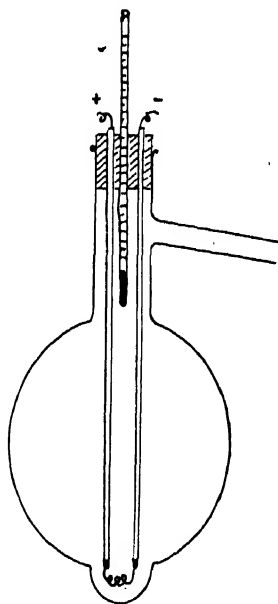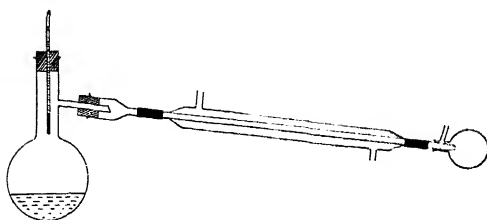
FIG. 2 (II *)

Fig. 2 (II *) shows the well-known apparatus for distillation into fractions, &c., while Fig. 3 (II *) illustrates an apparatus with ground-glass connexions.

Method of Fractional Distillation. The fractionation of a mixture of two liquids can best be explained by a concrete example (see Figs. 2 (II *) and 3 (II *)). A mixture of 100 grams of benzene (b.p. 80·2°) and 100 grams
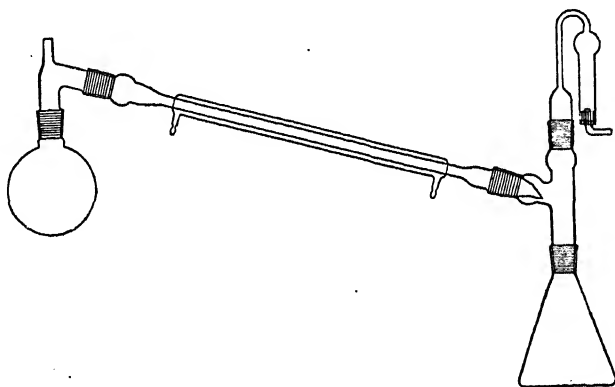
FIG. 3 (II *)

of toluene (b.p. 110·6°) was slowly distilled, and the distillate was collected in a convenient number of fractions, the receivers being changed when the boiling-point reached certain definite previously arranged temperatures, the actual readings being corrected for barometric pressure and for errors in the thermometer scale. The results of the first four fractionations, and also of the ninth, are given in the table on opposite page.

In the first distillation the temperature rose almost at once to 86° and the first portion of distillate was therefore collected in receiver 4. On the other hand, the temperature reached 110·6° before the whole of the liquid had come over; the residue, therefore, consisted of pure toluene.

The distillate in receiver 4 was now placed in a smaller flask and distilled, fractions being collected in receivers 2, 3 and 4. When the temperature reached 89·2 the flame was removed, and the contents of receiver 5 were added to the residue in the still. The distillation was recommenced, and fractions were collected in receivers 3, 4 and 5, the flame being removed when the temperature reached 92·2°. The distillation was continued in a similar manner until, after the addition of the contents of receiver 12, the temperature rose to 110·6°, when the residue of pure toluene was added to that from the first fractionation.

Number of receiver	Final temperature (corrected) = t	Weight of fraction = ΔW				t	ΔW
		I	II	III	IV	IX	
Pure benzene	—	—	—	—	—	80·2°	10·20
1	81·2	—	—	12·95	31·55	80·3	45·00
2	83·2	—	3·80	24·80	23·90	80·6	17·55
3	86·2	—	33·85	22·75	16·20	81·4	7·20
4	89·2	9·75	22·30	13·50	9·55	83·5	4·50
5	92·2	51·80	19·65	11·80	8·00	88·0	3·30
6	95·4	28·85	13·60	9·15	5·80	95·4	2·75
7	98·6	21·20	12·95	7·30	5·35	102·8	2·60
8	101·6	12·80	9·05	6·75	4·65	107·3	2·85
9	104·6	11·45	8·90	6·30	3·85	109·4	3·15
10	107·6	14·15	10·80	7·95	5·85	110·2	3·45
11	109·6	13·45	9·60	8·95	7·40	110·5	7·00
12	110·6	24·90	30·75	33·05	30·50	110·6	5·75
Pure toluene .	(110·6)	10·90	22·95	31·35	42·10	(110·6)	72·10

The third and fourth fractionations were carried out like the second. In the subsequent fractionations the temperature ranges of the middle fractions were gradually increased, and those of the lowest and highest fractions diminished. It was not until the ninth fractionation that pure benzene began to be collected. Eventually 81·4 grams of pure benzene and 88·8 grams of pure toluene were recovered.

In a considerable number of cases the boiling-point composition curve for a two-component mixture approximates to a straight line. The molecular composition of the vapour from the mixture is proportional to the partial vapour pressure of the components and is proportional to the product of the vapour pressure of the pure components and their concentrations in the mixture, if Raoult's law be assumed (partial vapour pressure of each component is equal to the product of the vapour pressure of the pure liquid and its concentration in the mixture). In most cases the vapour will be richer in the material of greater vapour pressure and separation of the components is possible.[1]

An example of this is afforded by the change in vapour pressure with composition of liquid oxygen-nitrogen mixtures. The total vapour pressure, P, is slightly less than the sum of the vapour pressures of oxygen and of nitrogen at the same temperature owing to their mutual solubilities. P changes in linear manner (curve BD) between the vapour pressure of nitrogen (curve BC) and that for oxygen (curve AD) as indicated in Fig. 4 (II *) (for 74·7° Absolute).

If x is the mol fraction of the more volatile component in the liquid and y that in the vapour, then

$$P = xp_n + p_0(1 - x)$$

This enables us to plot the total vapour pressure curve BD. On distillation

[1] From Reilly, *Distillation*, p. 3 (Methuen & Co., London).

the vapour will be richer in the more volatile component (nitrogen) as indicated in Fig. 5 (II *), which can be obtained knowing that

$$x = \frac{P - p_0}{p_n - p_0}$$

$$y = \frac{x p_n}{P}$$

where p_0 and p_n are the vapour pressures of oxygen and nitrogen at the particular temperature. (Raoult's Law being assumed.)
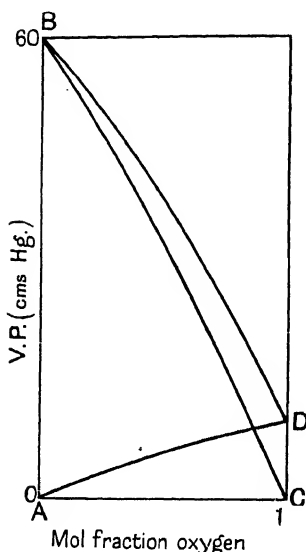

FIG. 4 (II *)
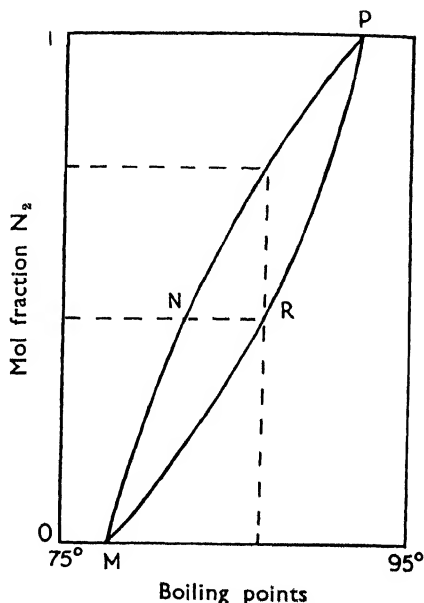
FIG. 5 (II *)

In the temperature-composition curve diagram, curve MNP shows the mol fraction of nitrogen in the vapour in equilibrium with different mixtures at the boiling-point. It will be observed that the nitrogen content of the liquid (curve MRP) throughout is less than that of the vapour with which it is in equilibrium. It is thus possible to effect the separation of the constituents by fractionation. A more detailed account of the fractionation of liquid oxygen-nitrogen mixtures is given by Brown.[1]

In the case where the vapour-pressure-composition curve exhibits a maximum or minimum point, then constant boiling-point or azeotropic mixtures are formed. This phenomenon is most general when one of the components of the mixture is a substance which exhibits association in the liquid state (e.g. hydroxyl compounds). The constant vapour-pressure mixtures are generally binary or ternary mixtures. For a list of known azeotropic mixtures reference should be made to Lecat's books, *La tension de vapeur des mélanges de liquides l'Azéotropisme* (Brussels, 1918) and

[1] *Trans. Chem. Eng. Congress*, London, 1936, Vol. II, p. 303.

Bibliographic de l'Azéotropisme (Brussels, 1932), or Young's *Distillation Principles and Processes* (London, 1922).

The formation of mixtures of maximum vapour pressure is very much more common than that of minimum vapour-pressure mixtures, and in the present discussion the former only will be considered.

In the case where the vapour pressure-composition curve exhibits a maximum, a mixture corresponding to this will boil at a lower temperature than any other mixture. On fractionation the mixture of minimum boiling-point distils over first at constant temperature and without variation in composition. Any excess of one or other of the components is left in the still. It is possible by repeated distillation or by distilling through a fractionating column to isolate the mixture of maximum vapour pressure and one of the components. An example of this is afforded by the production of rectified alcohol of 96·5 per cent concentration. In practice, vapours are fed to a fractionating column at about 40 per cent alcohol concentration from a column acting as an exhauster, as in the original Coffey still. Rectified spirit is drawn off a few plates below the top of the fractionating column. The more volatile head-products (acetaldehyde, &c.) are drawn from the top.

The physical methods of separating constant-boiling mixtures are divided into two classes by Sunier and Rosenblum.[1] Certain of these depend on difference of mass of the components. Atmolysis, non-equilibrium evaporation (see chapter on Fractionation), thermal diffusion and centrifuging processes have been suggested. Other methods involving vapour-pressure relations have found greater commercial applications. Among these are variation of pressure and addition of a third component, either a liquid to form other azeotropes or a solid which will change the vapour pressures of the components to a different degree depending on its solubility in the respective members of the system. The ' salting-out ' effect may be applied. Freezing may also be used as a method of separation. Silica gels have been found to break up azeotropic mixtures.[2]

Sunier and Rosenblum[3] have also drawn attention to the separation of constant-boiling mixtures by distillation under reduced pressure. The works of Roscoe and Ditmars[4] and of Hulett and Bonner[5] show that the composition of the constant-boiling hydrochloric acid varies with pressure, increasing from 18 per cent hydrogen chloride at 250 mm. to 23·2 per cent at 5 mm. pressure. The ethyl alcohol-water system allows of a much better separation into components.[6] At 760 mm. pressure the alcohol-water mixture contains 4·4 per cent water, but a complete separation takes place under a pressure of 70 mm. and 27·96° (the boiling-point of absolute alcohol under these conditions). Thus, fractionation of the minimum constant-boiling mixture at a moderately reduced pressure produces absolute alcohol. This fact is embodied in the Barbet patent[7] and in the earlier patents of Winter.[8] Similarly, almost complete separations have been effected for

[1] *Ind. Eng. Chem.*, Anal. Ed., 1930, *2*, 109.
[2] Grimm, *Z. angew. Chem.*, 1928, *41*, 98, 104.   [3] *Loc. cit.*
[4] *J. Chem. Soc.*, 1860, *12*, 136.   [5] *J. Amer. Chem. Soc.*, 1909, *31*, 390.
[6] Merriman, *J. Chem. Soc.*, 1913, *103*, 628.
[7] Patart, *Bull. Soc. encour. ind. nat.*, 1924, *136*, 188, 201.
[8] Winter, U.S. Patents 1427, 885–8, 1922.

the systems ethyl acetate-water, ethyl acetate-ethyl alcohol and ethyl acetate-alcohol-water.[1]

Although no binary mixture of alcohol and water is formed at reduced pressure (70 mm.), in practice anhydrous alcohol is not easily separated by distillation under reduced pressures. The difference between the boiling-points of absolute alcohol and e.g. 96 per cent spirit is extremely small. Under a pressure of 94·9 mm. the binary azeotrope containing 0·5 per cent of water has a boiling-point only 0·03° lower than that of pure alcohol, so that it is difficult to separate the azeotrope from the excess of alcohol. On the other hand, mixtures in which the ' effective components '[2] are (a) the binary azeotrope and (b) water (i.e. dilute aqueous solutions of alcohol) are relatively easily fractionated into the ' effective components ' since the boiling-points of these are now fairly widely separated. For a discussion of azeotrope formation, &c., see Hildebrant, *Solubility of Non-Electrolytes*, as well as the sections on distillation in the usual chemical engineering textbooks.
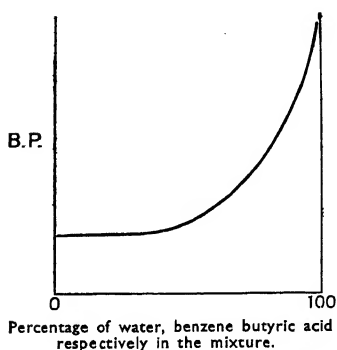

B.P.

0   100

Percentage of water, benzene butyric acid respectively in the mixture.

FIG. 6 (II *)

The behaviour of strong spirit under reduced pressure is similar to that of n-hexane containing a little benzene or that of dilute butyric acid (under normal pressure). It may be noted that in these cases the boiling-point-composition curves approximate to that shown in Fig. 6 (II *). The curve is nearly horizontal at the bottom, but rises sharply at the top. Separation of alcohol, n-hexane or water from the respective mixtures would be almost if not quite impossible, whereas that of water, benzene or butyric acid from mixtures rich in these substances can be effected.

Merriman[3] suggests that in a binary system the concentration of the component which has the lower rate of change of vapour pressure with temperature increases as the pressure under which the mixture exists is lowered. This is not the case for an ethyl alcohol-water mixture. In this connexion Wrewsky[4] and Tanaka and Kuwata[5] have pointed out that the concentration of the component with the greater heat of vaporization increases with increase of the superincumbent pressure in the case of azeotropic mixtures of the lower alcohols.

The technical utilization of the formation of azeotropic mixtures by the addition of a third component has important industrial application, and one example of this will be considered. In 1902, Young showed that when a mixture of ethyl alcohol, benzene and water was distilled, a tertiary mixture of minimum boiling-point was formed, and this distilled at a lower tempera-

[1] Merriman, *J. Chem. Soc.*, 1913, *103*, 1790.
[2] Cf. Reilly, Kelly, and Ryan, *J. Soc. Chem. Ind.*, 1937, *56*, 231T.
[3] Young, *Distillation Principles and Processes*, p. 61.
[4] *Z. Physik. Chem.*, 1912, *81*, 1; 1913, *83*, 551.
[5] *Chem. News*, 1927, *137*, 13; *J. Fac. Eng.*, Tokyo Imp. Univ., 1927, *17*, 117.

ture than the normal boiling-point of any of the binary mixtures of these substances or the boiling-point of the individual substances. The composition and boiling-points of all the constant-boiling-point mixtures formed from alcohol, water and benzene is shown in Table I.[1]

TABLE I

COMPOSITION AND BOILING-POINT OF CONSTANT BOILING-POINT ALCOHOL, WATER, BENZENE MIXTURES

Mixture	Boiling-point	Composition		
		Alcohol	Water	Benzene
	° C.	%	%	%
Water-alcohol-benzene	64·85	18·5	7·4	74·1
Alcohol-benzene . .	68·25	32·41	—	67·59
Water-benzene . .	69·25	—	8·83	91·17
Alcohol-water . .	78·15	95·57	4·43	—
Alcohol	78·3	100	—	—
Benzene	80·2	—	—	100
Water	100	—	100	—

When benzene, in controlled amounts, is added to the aqueous alcoholic solution and distilled at atmospheric pressure, the first product is a mixture of alcohol, benzene and water B.P. 64·85° (mixture containing 18·5 per cent alcohol, 7·4 per cent water and 74·1 per cent benzene). The next fraction being alcohol and benzene (azeotropic mixture B.P. 68·24° mixture containing 32·37 per cent alcohol). The final fraction is pure alcohol (B.P. 78·3°). The benzene can be recovered by dilution with water, &c.

It is interesting to note here that in the case of the three-component system—methyl alcohol, benzene and water [2]—no ternary azeotrope could be found to permit elimination of water by Young's method.

Craven [3] deals with the third component method in fractional distillation by considering the effect of the third component on the relative volatility of the two components it is desired to separate, and puts forward a tentative attempt to indicate the likely effect of submitting a binary mixture to a distillation using a counter-current stream of a third component down the column.

The original paper of Craven should be consulted for further extension of this method of attack.

For many years this method has been used to prepare absolute alcohol. In recent years, with the demand for 99–100 per cent ethyl alcohol to use in alcohol-petrol mixtures as a petrol substitute, there has been a great amount of research to find the best conditions, both in details of work and in modification of the minimum boiling-point mixture so as to procure a cheap anhydrous alcohol.[4]

The distillation of partially miscible liquids, e.g. normal and isobutyl

[1] From *J. Chem. Soc.*, 1902, *81*, 710.
[2] Barbaudy, *Ann. Combustibles liquids*, 1931, *6*, 228.
[3] *Ind. Chem.*, 1933, *9*, 414.   [4] Cf. Reilly, *Distillation*, London, 1936.

alcohol and water, ether and water, is interesting. The vapour pressure-composition curve for the latter case is shown in Fig. 7 (II *). The distillation of n-butyl alcohol on the industrial scale is considered by Reilly and Henley in Young's *Distillation Principles and Processes*, 1922, and *Biochem. J.*, 1920, *14*, 229.

OM is the vapour-pressure curve for an unsaturated solution of ether in water. When under ordinary conditions of temperature and pressure more than 7 per cent of ether is ad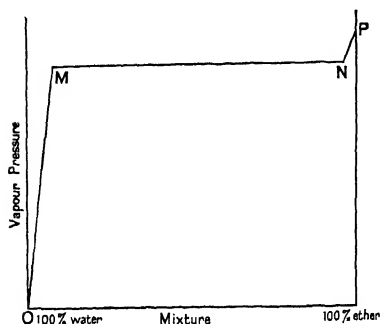ded to water, two layers are formed. The upper layer is a saturated solution of water in ether and the lower layer a saturated solution of ether in water. When both liquid layers are present, the system is monovariant and the mixture will distil at constant temperature, since for a given temperature the vapour pressure is fixed as well as the composition of the vapour phase and distillate over the range of compositions represented by MN. Addition of more ether merely alters the relative amounts of the two phases until (corresponding to the point N) enough ether has been added to dissolve all the water, when the boiling-point alters continuously with the composition as represented by NP. The total vapour pressure of the mixture is less than the sum of the vapour pressures of the pure components at the same temperature owing to the lowering due to the mutual solubilities.

FIG. 7 (II *)

In the case of a mixture of two completely insoluble liquids, the total vapour pressure will be the sum of the vapour pressures of the components. This case is dealt with in the chapter on steam distillation.

The boiling-range of petroleum products, including petrols, is usually determined by a standardized method, e.g. a method giving full instructions for the carrying out of this determination under fixed conditions is described in *Standard Methods of Testing Petroleum and its Products*, Inst. of Petroleum Technologists, London (1935).

A formula relating the boiling-points of petrols with their vapour pressures has been developed by Bridgeman, Aldrich and White.[1] With a fair degree of accuracy it holds for all grades of petrol when they are free from dissolved air and moisture. It is:

$$\log p = 6 \cdot 76 - 3 \cdot 88 \frac{N}{T}$$

where p = the vapour pressure in mm. Hg at temp. T° C. (absolute)

　　　N = the temperature at which bubbles commence to form in the water and air-free petrol at atmospheric pressure.

The term N is called the *normal bubble point* and is stated to be equivalent to the temperature at which 10 per cent (corrected for loss) has distilled over in the A.S.T.M. distillation test.[2]

[1] *Soc. Aut. Eng.*, 1929, *24*, 219.

[2] Spiers, *Technical Data on Fuel*, Nat. Comm. World Power Conference, London, 1935.

Vapour Pressure and Latent Heat. A number of equations have been obtained from the Clausius-Clapeyron formula (1) given on page 3. These are :

$$\frac{dp}{dT} = \frac{L}{R'T^2} \cdot p \quad . \qquad . \qquad . \qquad . \qquad . \quad (2)$$

$$\ln p = \frac{-L}{R'T} + \text{constant} \quad . \qquad . \qquad . \qquad . \quad (3)$$

$$\log_{10} p = \text{const.} - \frac{1}{T}\left(\frac{L}{1 \cdot 985 \times 2 \cdot 303}\right) \quad . \qquad . \qquad . \quad (4)$$

and over a small temperature interval

$$\log_{10} p_1 - \log_{10} p_2 = \frac{L}{4 \cdot 571}\left(\frac{I}{T_2} - \frac{I}{T_1}\right) \quad . \qquad . \qquad . \quad (5)$$

If the vapour pressure at a number of temperatures is determined and the values of log p are plotted against I/T, it will be seen from equation (4) that a straight line will be obtained.

The value of the constant in equation (4) is found by putting I/T equal to zero : that is, it is the intercept on the log p axis for I/T = 0 ; in practice it is best found by calculation from the slope of the curve. When the constant has been obtained, any pair of values of log p and I/T read from the curve will give the value of L, the latent heat of vaporization. L may also be obtained using (5) above and two pairs of values read from the curve. Vapour pressure-temperature data can be obtained from the usual tables. Kirchoff's vapour pressure equation is obtained on the integration of (2) above, if it is assumed that $L = L_0 + aT$.

$$\ln p = - L_0/R'T + a \ln T./R' + \text{constant}.$$

That is, as in Vol. I, p. 119 :

$$\log p = A - B/T - C \log T.$$

Hence, if T_1 and T_2 are the temperatures at which the saturated vapour pressures are the same for two substances 1 and 2, and if we neglect the term C log T, we have

$$B_1/T_1 = B_2/T_2 + A_1 - A_2 \quad . \qquad . \qquad . \qquad . \quad (6)$$

If T_1, T_1' for substance 1 and T_2, T_2' for substance 2 are absolute temperatures at which the vapour-pressure is p, p' respectively, then (cf. I, p. 120)

$$\frac{T_1'}{T_1} = \frac{B_2/T_2 + A_1 - A_2}{B_2/T_2' + A_1 - A_2}$$

$$\frac{T_1 - T_1'}{T_2 - T_2'} = \frac{B_1}{B_2} \cdot \frac{(A_2 - \log p)(A_2 - \log p')}{(A_1 - \log p)(A_1 - \log p')}$$

Hence if $A_1 = A_2$ (for chemically similar substances), we have

Ramsay-Young : $T_1'/T_1 = T_2'/T_2$
Dühring : $(T_1 - T_1')/(T_2 - T_2') = \text{constant}$

(6) gives a useful straight-line relationship especially where one of the substances 1 or 2 is taken to be water. Perry and Smith [1] describe a linear rule and in addition to testing it for vapour pressures and latent heats of vaporization apply it to other properties, viz. electrolytic conductance, heat capacities, Joule-Thomson effects, gas solubilities, &c.

Other straight-line relationships suitable for wide ranges of temperature can be obtained by plotting logs of the vapour pressure ($\log p$) against reciprocals of the absolute temperatures ($1/T$) or by plotting $\log p$ against $\log T$. Another method is due to Cox [2] which is equivalent to assuming [3] that the vapour pressure of a substance is represented by the equation

$$\log p = A - \frac{B}{t + 230}$$

where p is the vapour pressure, t the temperature in ° C.; A and B constants. By plotting $\log p$ against $1/(t + 230)$ a straight line is obtained for which, in the usual way, two experimental values are sufficient.

The latent heat of vaporization, l, at any temperature T is defined as the number of calories required to convert 1 gram of the liquid at temperature T into vapour at the same temperature. The term is commonly used for the special case when boiling takes place at atmospheric pressure. The molecular heat of vaporization L at a temperature T is the number of calories required to convert 1 gram molecule of liquid at T into the vapour state at the same temperature.

The latent heat is made up of two parts ; firstly, the work done in overcoming the external pressure, and secondly, the work done in separating the molecules. For a gram molecule the external work is

$$A = p(v - v'),$$

where p is the pressure, v the volume of a gram molecule in the gaseous state, and v' that in the liquid state ; i.e. v and v' are the molecular volumes. If the pressure is not large, v' is negligible compared with v, and the external work

$$A = pv = RT$$

That is, the external work is independent of the nature of the liquid and depends only on the temperature. The internal work varies with the nature of the liquid.

The decrease in the total energy

$$U = RT - JL$$

therefore

$$\frac{dU}{dT} = R - J\frac{dL}{dT}$$

but the rate of decrease in the total energy is equal to the difference of the molecular heats in the two states, multiplied by the mechanical equivalent of heat,

$$\frac{1}{J}\frac{dU}{dT} = M.c - C_v$$

[1] *Ind. Eng. Chem.*, 1933, *25*, 195.   [2] *Ibid.*, 1923, *15*, 592.
[3] Calingaert and Davis, *ibid.*, 1925, *17*, 1287.

where c is the specific heat per gram of liquid, and C_v is the molecular heat of the gas at constant volume;

therefore
$$\frac{R}{J} - \frac{dL}{dT} = M.c - C_v$$

but
$$R/J = C_p - C_v$$

therefore
$$\frac{dL}{dT} = C_p - M.c$$

This expression gives the rate of change of latent heat with temperature. Since in all cases the specific heat in the liquid state is greater than that in the gaseous state, the latent heat always decreases with rise of temperature; and this is to be expected because it must become zero at the critical temperature.

The second law of thermodynamics gives an important relationship between the latent heat of vaporization and the change of vapour pressure with temperature. If A is the external work,

$$A - U = T.\frac{dA}{dT}$$

Working with 1 gram of liquid,

$$A = p(V - V')$$

$$\frac{dA}{dT} = \frac{dp}{dT}(V - V')$$

$$U = p(V - V') - Jl$$

where V is the volume of 1 gram (specific volume) of gas at pressure p and temperature T, V' is the specific volume of the liquid and l is the latent heat per gram;

therefore
$$Jl = T.\frac{dp}{dT}(v - v')$$

This is the well-known Clausius-Clapeyron equation and enables us, for example, to calculate the latent heat from the slope of the vapour-pressure curve, or, conversely, to find the effect of change of pressure on the boiling-point from the latent heat. Neglecting v' we have

$$\frac{JL}{T} = \frac{dp}{dT}.v = \frac{RT}{p}.\frac{dp}{dT} = R.\frac{d \ln p}{d \ln T}$$

according to Van der Waals the expression $\dfrac{d \log p}{d \log T}$ should be constant at corresponding states, and Guldberg has pointed out that the boiling-point at atmospheric pressure is equal to two-thirds of the critical temperature when both are measured on the absolute scale, so that the boiling-points at atmospheric pressure are corresponding temperatures; hence L/T is a constant when T is the boiling-point (° A.) at atmospheric pressure.

Trouton found that for non-associated liquids L/T = 21 (Trouton's rule). For associated liquids such as water, greater values are obtained. This rule is taken to hold in the McCabe and Thiele method for plate calculations.[1]

[1] *Ind. Eng. Chem.*, 1925, *17*, 605. On Trouton's rule see Vol I, pp. 116, 118.

Liquid-Vapour Equilibrium (x-y) Curves

These can be obtained from Raoult's law in some cases. For the experimental determination of equilibria data for the compositions of liquid and vapour in contact, see Young, *Distillation Principles and Processes* (London, 1922). A recent determination of data for the system ethyl alcohol-water (as well as methyl alcohol-water and acetic acid-water) has been made by Cornell and Montonna,[1] and Fig. 8 (II *) from this article shows plotted the data of various workers.[2] It will be noted that the
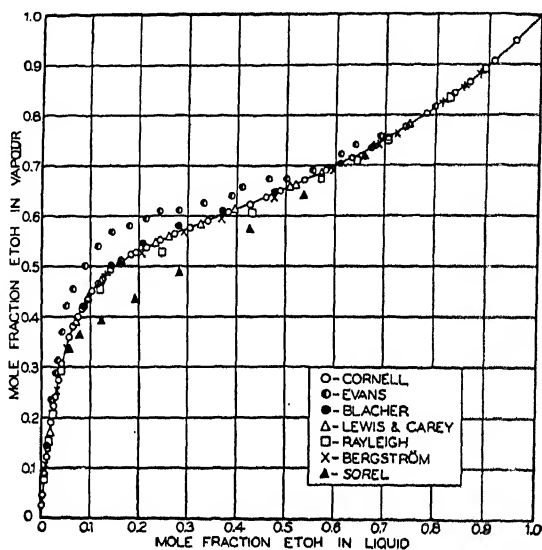
FIG. 8 (II *)

curve cuts the diagonal, thus indicating the existence of a constant boiling-point mixture. An apparatus for the determination of the composition of vapours from boiling binary solutions is described by Othmer[3] and is suitable for the design of engineering equipment. Another ' equilibrium still ' is described by Mizuta.[4]

Fugacity.—The fugacity, *f*, of a substance is defined by the equation

$$F = RT \ln f + \text{constant}$$

F is the ' free energy ' and the constant is a function of T only. See Lewis and Randall, *Thermodynamics*. The fugacity of a substance represents a corrected vapour pressure, *p*, when the vapour is a perfect gas. The difference between *f* and *p* is a measure of the divergence of the gas from the ideal perfect gas.

[1] *Ind. Eng. Chem.*, 1933, *25*, 1331.
[2] For detailed reference to the various workers named in Fig. 8 (II *), see Cornell and Montonna's paper, *loc. cit.*
[3] *Ind. Eng. Chem.*, Anal. Ed., 1932, *4*, 232.
[4] *J. Soc. Chem. Ind., Japan*, 1934, *37*, 11.

SECTION 2: FRACTIONATION [1]

In fractionating, use is made of columns or still-heads to complete the separation of the constituents in one operation (e.g. with certain binary mixtures) in place of several distillations into fractions. In industry, fractionating columns or towers may be (1) Sieve plate columns, (2) Bubble-cap plate columns, (3) Packed columns. When used in a continuous process, the feed to the columns is liquid heated to near the boiling-point or partly liquid and vapour and enters above the end of the column, the lower plates acting as stripping plates and removing the last traces of the more volatile component. Each plate acts in effect as a still, the composition of the liquid and vapour in its neighbourhood remaining fairly constant so that a product of definite composition may be drawn off from any plate. Near the top of the column, the concentration of the more volatile component is high. The heat necessary for vaporization occurring on each plate is provided by condensation of ascending vapours, while at the end, other means are provided.

The separation of the constituents in an industrial column is dependent on the provision of reflux, i.e. return of part of the condensate down the lagged column. Broadly speaking, reflux at any point in the column will be richer in the more volatile component than the immediately ascending vapours; condensation of relatively greater amounts of the less volatile component will occur, followed by vaporization of material richer in the more volatile component; the less volatile component being 'washed' out of the vapour.

Fractionating columns may also be used in an intermittent manner. In this case the feed will be in the form of vapour from the mixture heated in a separate vessel and introduced at the column end. The composition of the liquid in the vessel, the vapours entering the column and throughout the column will vary continuously with the progress of the distillation. This is the case in the usual laboratory fractionations employing ordinary still-heads.

In a simple laboratory unlagged rectifying column fractionation is mostly effected by partial condensation; vapour enrichment following partial condensation. A certain amount of rectification by interchange between reflux and vapour may occur in parts of the column. The design of intermittent and continuous columns for industrial fractionation is described in textbooks on chemical engineering. In this connexion the papers on distillation of the *Transactions of the Chemical Engineering Congress* (London, 1936), should also be consulted.

Bubble-cap plate towers are widely used in industry and their construction ensures thorough washing of the reflux by the ascending vapours

[1] *Cf.* Reilly, *Distillation*, Chap. 1 (Methuen & Co.), 1936.

ensuring practically complete equilibrium. Fig. 9 (II *) shows a section of a bubble-cap plate tower.

A simple laboratory column comparable to the bubbling-cap type industrial column is described by Palkin.[1] This is illustrated in Fig. 10 (II *). It is capable of handling large columns of vapour without undue tendency to flooding, and is suggested to be of value in vacuum work. The screen (gauze plate) consisted of nickel wire gauge. Messrs. The Thermal Syndicate, Ltd., have constructed a working model of a full-sized bubble-cap rectifying
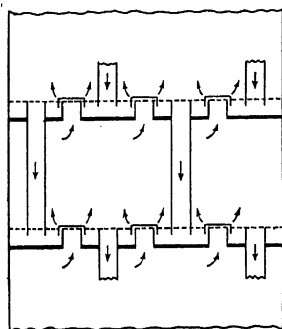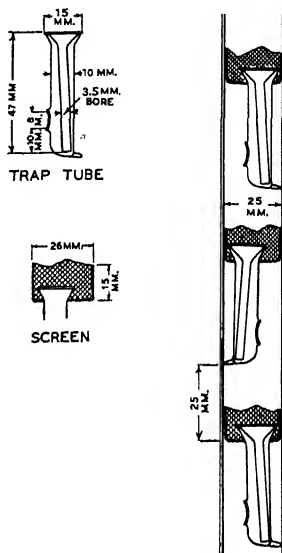

FIG. 9 (II *)

FIG. 10 (II *)

column in fused quartz. The column is 1 foot 7 inches long (approx.). It can be used for continuous or batch distillations and is specially suitable for fractionations at high temperatures. Liquid can be drawn from any of the plates while vapour samples or temperatures can be got from other exits. The column is also suitable for small-scale industrial fractionation of liquids which boil at high temperatures and which are required in an exceedingly high degree of purity.

The design of packed columns is discussed by Peters,[2] Calingaert and Huggins,[3] and Fenske, Tongberg and Quiggle.[4] In comparing columns it is usual to relate the separation obtained by one theoretically perfect bubble plate to the height of column which will effect the same amount of rectification at a given reflux ratio. This gives the H.E.T.P. (height equivalent to a theoretical plate). It is obtained from analysis of the distillate and liquid in the still and from liquid-vapour equilibrium data.[5] More recently the concept of the 'transfer unit' and the H.T.U. (height of a transfer unit) has been employed.[6]

In industrial columns, generally, even washing and distribution of the reflux, vapour velocity and pressure drop, as well as the amount of liquid held up as reflux in the column, are of importance. In packed columns the pressure drop and amount of liquid hold-up is relatively low, and these

[1] *Ind. Eng. Chem.*, Anal. Ed., 1931, *3*, 377.   [2] *Ibid.*, 1922, *14*, 476.
[3] *Ibid.*, 1924, *16*, 585.   [4] *Ibid.*, 1934, *26*, 1169.   [5] See Peters, *loc. cit.*
[6] Cf. Chilton and Colburn, *Ind. Eng. Chem.*, 1935, *27*, 255, and Baker, *ibid.*, 1935, *27*, 977.

columns are of value in the vacuum fractionation of mixtures containing components boiling at high temperatures and with boiling-points close together.

The 'true-boiling-point' distillation curve of petroleum crudes has proved of value in petroleum work.[1] This distillation is similar to the Engler distillation of petroleum fractions, but the flask is provided with an efficient fractionating column. A suitable true-boiling-point still is described by Beiswenger and Child.[2] See also papers by Podbielniak (reference later). It may be mentioned here that vacuum fractionation must replace the standard Engler or A.S.T.M. apparatus for fractions boiling above 750° F. Apparatus for this work is described by Peterkin and Ferris.[3]

The efficiencies of the usual type of laboratory columns (see Fig. 11 (II *)) were compared by Hill and Ferris using carbon tetrachloride-benzene mixture.[4] They found a simple packed column using 'Jack chain' to

Plain Tube   Wurtz   Glinsky   Young
        Pear   Lebel-
                    Henniger   Vigreux   Snyder
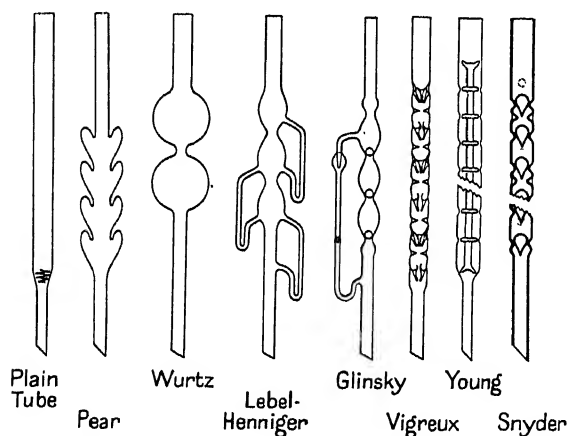
FIG. 11 (II *)

be comparable with more elaborate glass columns. They also give a convenient method for comparing laboratory columns. Fig. 12 (II *) shows one section of the Modified Young Evaporator Still-head. The fragile funnel on three legs is dispensed with, and the top of the middle tube a is blown into a flattened bulb, a'. The drops of liquid from the depression above fall on a' and then spread themselves over the surface of the tube. When rapid separation is taking place the liquid flowing down the sides of the inverted tube breaks up into streams. The evaporator still-head is highly efficient for the purification of small quantities of liquid of moderate boiling-point.

The design of a laboratory Hempel column is examined by Marshall and Sutherland.[5] The unlagged column (i.e. where vapour enrichment is

[1] Lewis and others, *Amer. Petrol. Inst. Bull.*, 1930, *11*, 73; *Trans. Amer. Inst. Chem. Eng.*, 1928.

[2] *Ind. Eng. Chem.*, Anal. Ed., 1930, *2*, 284.

[3] *Ibid.*, 1925, *17*, 1249; Watson and Wirth, *ibid.*, Anal. Ed., 1935, 7, 72.

[4] *Ibid.*, 1927, *19*, 379.   [5] *Ibid.*, 1927, *19*, 735.

provided for mostly by partial condensation in the column) is compared with the lagged column provided with reflux taken from the distillate. The effectiveness is much better in the latter case. MacIntyre [1] describes a convenient reflux regulator. For other laboratory reflux regulating devices, see later.

The construction and use of Raschig laboratory columns is discussed by Evans and others.[2] A column (3 feet long) suitable for vacuum distillation of fatty acids as well as a 6-foot column for alcohol rectification are described.

Snethlage [3] describes a laboratory column for giving 100 per cent methyl alcohol from water containing not less than 4 per cent, the chief feature of which is the means for accurately regulating the cooling of the dephlegmator. It may be pointed out here that even distribution of the reflux does not seem to be so necessary in laboratory columns, as it has been shown by Marshall and Sunderland [4] that wide variations in liquid and vapour velocity show but little effect on fractionating efficiency for laboratory columns.

FIG. 12 (II *)

The design of laboratory columns is also dealt with by Podbielniak (see references later). For semi-large-scale fractionating equipment the apparatus of Tongberg, Quiggle and Fenske [5] should be suitable. The 'Vulcan Copper and Supply Co.', of Cincinnati, Ohio, U.S.A., have as a standard an adaptable apparatus for the study of distillation problems and which is suitable for vacuum or pressure work.

An apparatus and technique for the separation by distillation of arsenic, antimony, and tin from one another and other elements having non-volatile chlorides has been described by Scherrer.[6] The apparatus is made entirely of glass (arsenic trichloride has a B.P. 130°, antimony trichloride 220·2°, and stannic chloride 114°). Germanium tetrachloride can also be distilled under similar conditions to arsenic.

A description of a semi-large-scale experimental fractionation plant installed at the Royal Technical College, Glasgow, is described in *Ind. Chem.*, 1935, *11*, 441.

A convenient series of distillation apparatus based on Burger's original design have lately been made available by Firma Wilh. K. Heinz, Stützerbach, Thüringen, Germany. Figs. 13 (II *) a and 13 (II *) b show two forms of this series of apparatus. Fig. 13 (II *) a shows a simple type of apparatus which is suitable for the distillation of high boiling substances under ordinary or reduced pressure. The column, 1, can be lagged with asbestos cord and filled with a suitable filling material, e.g. short glass tubes, Lessing rings, &c., which can be supported on a perforated plate, 2, of porcelain or platinum. The air capillary is inserted at 4. The splash-

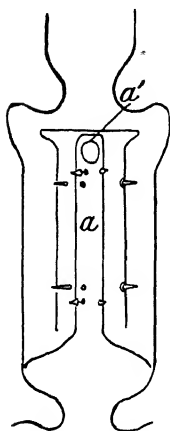[1] *Chem. Ind.*, 1933, *52*, 578R, 618R.
[2] *Ind. Eng. Chem.*, Anal. Ed., 1930, *2*, 339.   [3] *Chem. Wkbd.*, 1934, *31*, 748.
[4] *Ind. Eng. Chem.*, 1927, *19*, 735.   [5] *Ibid.*, 1934, *26*, 1214.
[6] *J. Res. Nat. Bur. Stand.*, 1936, *16*, 253.

head, 5, and the return tube, 6, serve to control the distillation of liquids which have even considerable tendency to frothing. The distillate tube, 7, is long enough to form the inner tube of a Liebig condenser. Tubulures 3 and 3′ serve for filling and holding the thermometer respectively. In Fig. 13 (II *) *b* an apparatus of this series is also shown which can, in addition to its use as a fractionator under ordinary or reduced pressure, be used as an extractor or reflux boiler under similar conditions. This particular apparatus is of value in esterifications and the like in which case the cylinder 3 can be packed with a dehydrating agent, the 3-way tap at 2 providing for the return of the dehydrated material to the reaction flask or its transference to the distillate receivers as required. A vacuum-jacketed fractionating column which gives sharp separations of small samples of closely boiling mixtures is made by Griffin & Tatlock (London). It is also designed with other modifications, e.g. with liquid air-jacketed reflux heads. Such an apparatus in the form of a vacuum-jacketed Dufton spiral was used by A. J. Gooderham [1] for use in connexion with the analysis of relatively small amounts of benzoles obtained from coal gas by active charcoal,[2] by wash oils, or by low temperature condensation.

(a)   (b)
FIG. 13 (II *)

The designer points out that the Dufton fractionating column [3] is capable of giving good separations of liquid mixtures and that it was recommended for analysis of benzoles,[4] but has, apparently, been rarely used as, even with good lagging, it is apt to choke at temperatures above 100°. By surrounding a Dufton spiral with a silvered vacuum jacket, it was found possible to obtain extremely sharp separations up to high temperatures. Fig. 14 (II *) illustrates two forms of such a fractionating column, one (Type 1) with the complete apparatus for a distillation. The fractionating surface consists of a spiral of 10–12 mm. pitch made by winding a soft 16 gauge (S.W.G.) wire, such as softened copper, around a stiff core (e.g. nichrome) of 18 S.W.G.
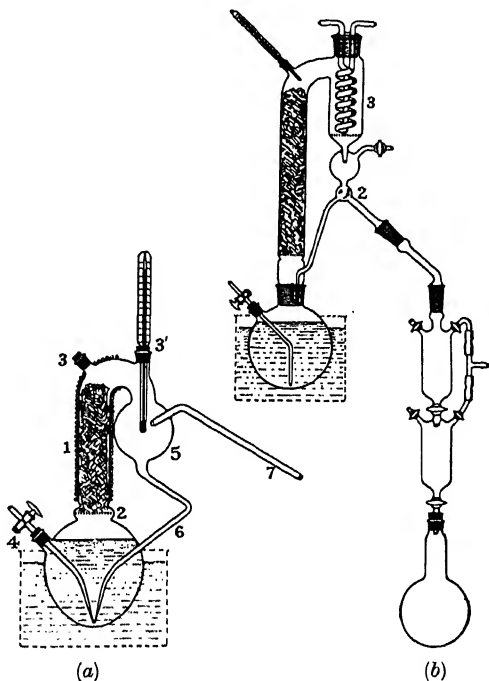
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[1] *J. Soc. Chem. Ind.*, 1935, *54*, 297T.
[2] *Cf.* Hollings, Pexton and Chaplin, *Trans. Inst. Chem. Eng.*, 1929, *7*, 85.
[3] *J. Soc. Chem. Ind.*, 1919, *38*, 45T.
[4] *Cf. Motor Benzole*, National Benzole Association, p. 604.

This spiral makes a tight, sliding fit in a strong tube of internal diameter 4·5 mm. which is surrounded by a silvered evacuated jacket. Gooderham recommends that the latter should have been evacuated by the methods of Scott, Cook, and Brickwedde,[1] or alternatively should be continuously evacuated during each distillation by a mercury-vapour pump—with backing pump —fitted on with a standard ground-glass joint.

Fig. 15 (II *) shows a fractionation curve obtained with this column for a mixture of 4 ml. each of benzene, toluene, and m-xylene. The steep slopes of the curves between the fractions are of interest and show the very sharp and almost theoretical separations obtained. The curve is displaced slightly to the left of the theoretical owing to the fact that a small volume of liquid is retained in the space between the thermo-couple (recording the distillation temperature) and the measuring cylinder. The column may also be used in other distillation work.

Reflux Regulation

Lewis[2] has shown that the reflux ratio (mols of vapour returned as refluxed liquid to the rectifying column per unit time divided by the mols of final product per unit time) must always be maintained above a certain minimum value in order to obtain a certain degree of fractionation. For distillation generally, a high efficiency of separation is obtained by using a large reflux ratio and a small rate of distillation.[3]

FIG. 14 (II *)

In the ordinary vacuum distillation apparatus rectification and reflux is provided by partial condensation of the vapours in the upper parts of the distillation flask or column (dephlegmation). More precise apparatus has, however, been recently evolved which can provide a definite reflux ratio (e.g. to return a definite amount of distillate down a lagged column and effect fractionation by interchange between reflux and vapour). Many other fractional distillation apparatus of this type have been described, e.g. by Bruun,[4] Schwartz and Bush.[5]

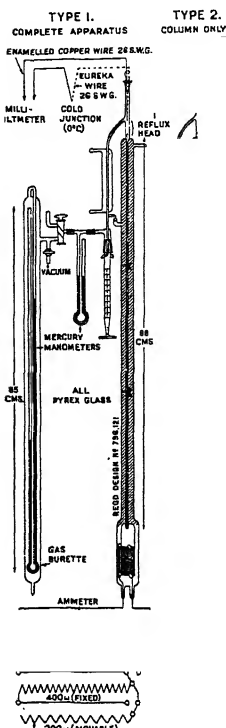
FIG. 15 (II *)
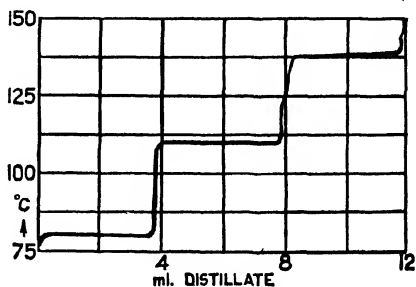
[1] *Bur. Stand. J. Res.*, 1931, 7, 935.   [2] *Ind. Eng. Chem.*, 1922, 14, 492.
[3] *Cf.* Shirk and Montonna, *ibid.*, 1927, 19, 907.
[4] *Ibid.*, Anal. Ed., 1930, 2, 187.   [5] *Ibid.*, 1931, 3, 138 ; 1932, 4, 142.

The apparatus described in the latter paper is shown in Fig. 16 (II *). The pyrex tube B (30 mm. in diameter) is held inside the evacuated jacket C (45 mm. internal diameter) by rubber stoppers. B is wound with a helix of chromel wire on a narrow strip of asbestos paper, fastened at the ends with copper wire. This arrangement avoids excessive condensation in the column. Generally speaking, in low-pressure fractionation the insulation of the column by means of magnesia or with an evacuated jacket is not satisfactory if the column is long. For a column 50 cm. long fifty turns of chromel wire should be sufficient. Thermometers are tied to small glass hooks on the column to enable the heating to be controlled. The column itself may be either the Vigreux or the packed type (suitable packing should be glass beads, Lessing rings, 'jack chain', &c.). The designers have had success with a 12-mm. tube filled with small jack chain by hanging two or three lengths from a metal ring at the top A.

The parts between G and G_1 represent the reflux regulator. By raising and lowering the amount of mercury in this the amount of reflux may be regulated. J is a heavy-walled rubber tube plugged at the lower end. K is a steel collar (1 cm. wide) fitted with a nut M. The rubber to glass connexions are sealed with shellac. L is a steel plate (8 cm. wide) and is put in place with the side arm test-tube H. The screw N, with the nut P adjusted, is connected with the nut M through the side arm and the rubber tube O. The valve is filled with mercury through F and the tube G. The test-tube H is filled with mercury through the funnel Q. This arrangement prevents leaks through the valve (it is well to scrub out J before putting in place to facilitate the removal of absorbed air).
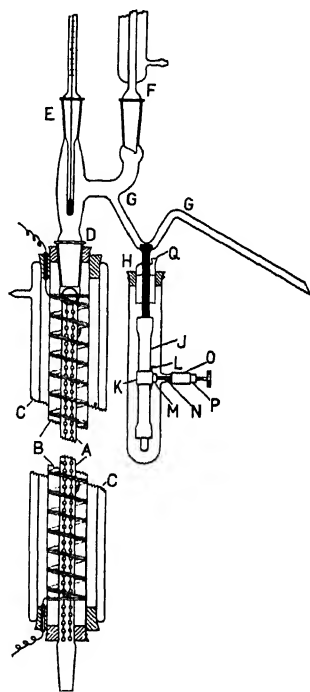
FIG. 16 (II *)

To collect the distillate fraction, the designers recommend a slight modification of the Bredt-Parlatosche 'star' [1] in which the receivers are either bulbs or test-tubes as contamination with stop-cock grease is overcome.

To carry out a fractionation, the column is first warmed to about 5° below the initial boiling temperature and the flask carrying a very fine capillary ebullition tube is put in place. The rate of distillation is controlled by the temperature of the heating bath. As the temperature of distillation rises the column is heated more strongly. The amount of reflux is regulated and the fractions taken according to the temperature readings on the thermometer at E. A typical fractionation curve is shown in Fig. 17 (II *). The esters were fractionated at 8 mm. pressure.

[1] *Cf.* Houben-Weyl, *Die Methoden der organischen chemie*, 2nd Ed., vol. I, p. 568.

The apparatus is suitable for amounts of liquid from 40 to 400 ml. having a boiling-point up to about 200° at pressures down to 1 mm.
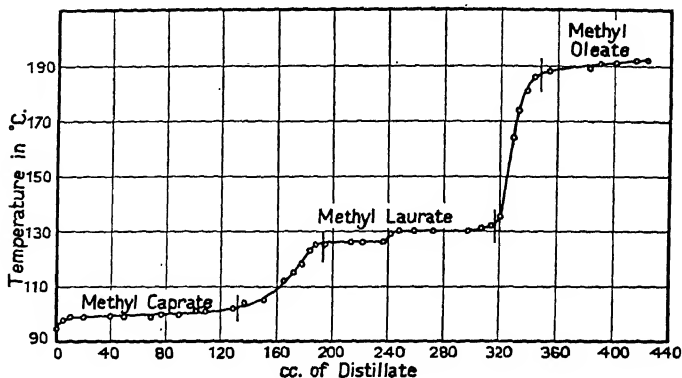
FIG. 17 (II *)

The reflux regulators described by Bruun [1] are also convenient. In Fig. 18 (II *) is shown a regulator (described in the above paper) for use on stills for which a definite and constant reflux ratio is desired. The vapour leaves the rectifying column at A. By means of a condenser B it is completely condensed into the bulb C. The capillary tube R enables an aliquot part of the condensate to be returned to the column. The remainder passes through the capillary D via the cooler H to the receiver.
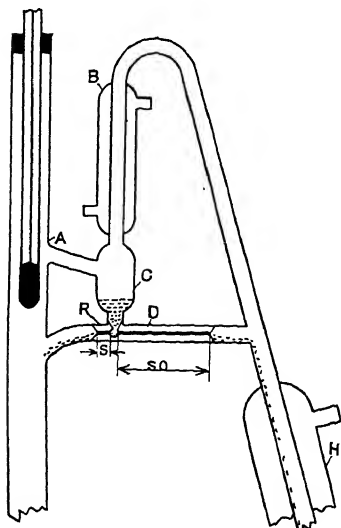
FIG. 18 (II *)

In order to obtain a definite and constant reflux ratio, the capillary tubes R and D are made of the same bore, but their lengths (S and SD respectively) are made inversely proportional to the amounts of liquid which must pass through them. For instance, if $R = 5$ and $D = 50$, the volume of reflux returned to the column divided by the volume of distillate will be 10 (reflux ratio). It is also possible to have R and D of nearly the same length but, of course, of different bores. To obtain the appropriate lengths of the two different sizes of capillary tubes, these are sealed horizontally to a vertical glass T-piece. Liquid is then run through the T-tube and the flow per unit time is measured for both capillaries. The lengths of the capillaries are then gradually adjusted until the desired amount of liquid per unit time passes through them. The regulator described above will maintain a constant reflux ratio at any rate of distillation. By placing

[1] *Loc. cit.*

a heating coil around the capillary D and thus increasing the flow through D by decreasing the viscosity of the liquid a certain amount of flexibility in the reflux ratio can be obtained. The rate of distillation is also indicated by the device since the rate is directly proportional to the height of the liquid in C. This bulb can be provided with a vertical scale on which each mark corresponds to a definite rate of distillation.

Bruun [1] also describes a reflux regulator for measuring and maintaining any desired constant reflux ratio. This is shown in Fig. 19 (II *). It can be used with convenience where liquids of varied character are to be distilled as well as for determining the best value for reflux ratio for different work involving extensive distillation. The vapour leaves the rectifying column at A and is condensed into the bulb C. A certain amount of condensate is returned to the column through a stopcock R and a capillary flowmeter E, and the other part through the capillary tube D, to the condenser H, and then to the receiver. The proportion of reflux to distillate may be regulated by adjustment of R and a quantitative measure of the reflux can be obtained at any time by observing the position of the liquid meniscus above E. The calibration of this flowmeter for any liquid is carried out by turning the three-way stopcock G, and collecting and measuring the liquid obtained during a short interval of time. For a given setting of R the position of

FIG. 19 (II *)

the liquid meniscus above E is also a sensitive index of the rate of distillation. The tube which carries the reflux back into the fractionating column is surrounded by a heating coil P in order to raise the liquid to near its boiling-point. In place of the capillary tube D a stopcock may be substituted in order to give a somewhat greater variation in the reflux ratios obtainable, but this method renders the distillate liable to contamination by the stopcock lubricating grease.
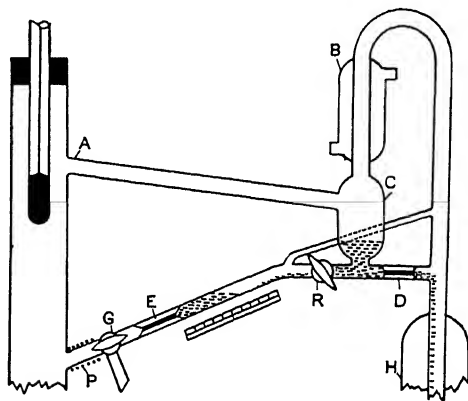
In both the above devices there is a free and unconstricted passage between the vapour outlet A and the condenser H which render the regulators suitable for vacuum distillations as well as for distillations at atmospheric pressure. The designer has used the regulators with bubbling cap-plate columns [2] as with a packed column using iron 'jack-chain' as a filling material.

Hickman [3] has designed a fractionating apparatus with self-contained 'auto-manometer' which is suitable for vacuum distillations and for obtaining true boiling-points at low pressures. In this apparatus the vapours pass through a large thermometer chamber and then enter a vapour diffusion pump in which they generate their own (nearly perfect) reference

[1] *Loc. cit.*   [2] *Ind. Eng. Chem., Anal. Ed.,* 1929, *1*, 212.   [3] *Loc. cit.*

vacuum. True boiling-points (i.e. boiling-points at pressures which are exactly known) under nearly perfect vacuum are obtained at the thermometer (see Fig. 20 (II *) b). This is suitable for liquids with high boiling-points ('phlegmatic') and for distillations from 1 mm. to 0·1 mm. with automanometer. For liquids with moderate boiling-points the apparatus in Fig. 20 (II *) a is suitable. The largest cavity of the dephlegmating column contains the thermometer bulb and the shorter arm of the auto-manometer. The longer arm reaches to the top of the condensing column which may be water-cooled. The manometer liquid in the automanometer is, of course, the distillate. The correct boiling-point at regions of rapid change of boiling-point is secured by stopping the exit tube so that the distillate flows back down the column. The pressure in the thermometer cavity (i.e. the exact pressure at which the material boils) is the sum of the pressure in an external manometer and the automanometer. The liquid in the automanometer requires scavenging frequently if the condensate varies in volatility or density as the distillation proceeds. In the case of the latter apparatus, suitable for down to 2 mm. of mercury, the 'reference vacuum' for the automanometer is conveniently given by a butyl phthalate manometer.[1] The apparatus described by Hickman can be obtained from Messrs. Fisher, of Pittsburg and Montreal. The necessity for separately determining the pressure in the space occupied by the thermometer is due to the fact that the pressure in this region is greater than that registered by an external manometer coming after the condenser and distillate collector in the usual apparatus. An excess of pressure is necessary to drive over the vapours.
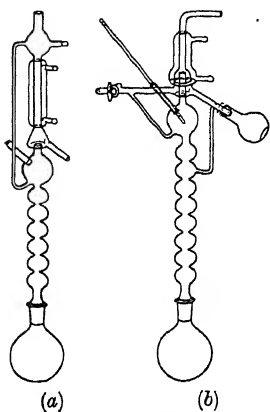
(a)   (b)

FIG. 20 (II *)

Laboratory apparatus in which a McLeod gauge is connected directly to the distillation flask has also been devised.[2] Condensation of vapours in the McLeod gauge is prevented by a trap cooled with liquid air or solid carbon dioxide.

A very complete investigation on the theory and methods of precise fractional distillation is described by Podbielniak[3] in papers read before A.C.S. meeting (Petroleum division), Chicago, September 1933—published later in *Ind. Eng. Chem.*, Anal. Ed. In this, apparatus is described suitable for fractionation of compounds of boiling-point ranging from — 180° to 100° and from 0° to 500°. Various indicating and control devices are also described, including automatic recording instruments. Fig. 21 (II *) shows curves illustrating analyses using low-temperature fractional distillation.

[1] *Cf.* Hickman, *J. Amer. Chem. Soc.*, 1930, 52, 4728.

[2] Davis and Hornberg, *Natl. Petr. News*, 1933, 25, 65, and Watson and Wirth, *Ind. Eng. Chem.*, Anal. Ed., 1935, 7, 72.

[3] *Ind. Eng. Chem.*, Anal. Ed., 1931 (part 1), 3, 177 ; 1933 (parts 2 and 3), 5, 119; 1933 (part 4), 5, 172.
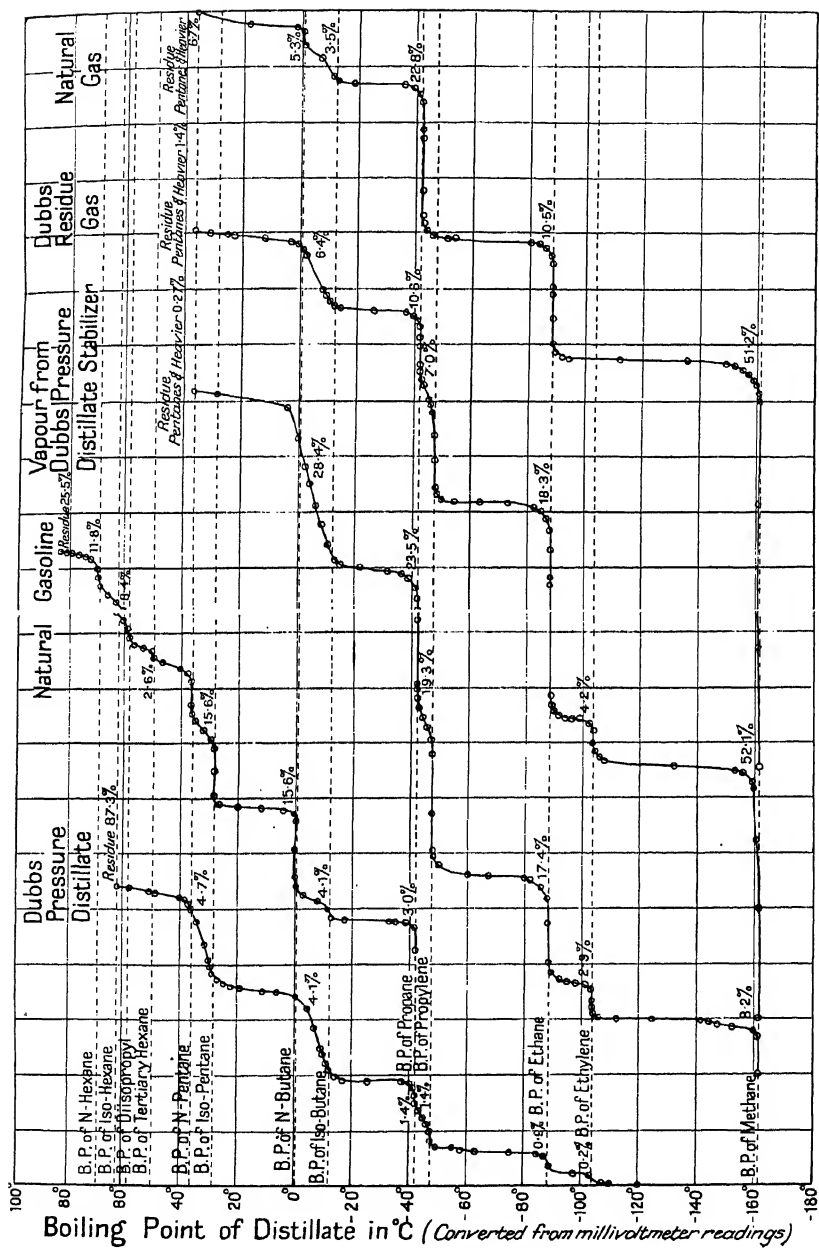
Volume of Distillate in Vapour Form

FIG. 91 (TT*)

In this apparatus an insulated specially designed fractionating column is employed. The constituents of low boiling-point are condensed by liquid air. The distillate is collected in the vapour state and measured under reduced pressure.

The apparatus can be obtained from Messrs. Podbielniak, Industrial Research and Analytical Laboratories, Chicago, U.S.A.; and seems to be of considerable value in the analyses of petroleums, industrial solvents, alcohol, &c. A 'short cut' routine method for analysis of hydrocarbons is described by Happel and Robertson.[1] An 'inverted' fractional distillation method is described by Bosselart,[2] while a fractional condensation method is due to Tropsch and Mattox.[3]

In connexion with the curves obtained by plotting boiling-point against volume-distilled-over, it may be mentioned here that Ginnings [4] has suggested the plotting of dV/dT against T in place of V against T. In this method the boiling-point of each component is a sharp maximum.

Micro Fractionation

Micro vacuum distillation technique is discussed by Smith.[5] An apparatus designed by Cooper and Fasce [6] is described below (Fig. 22 (II*)).

This apparatus enables quantitative separation to be effected under reduced pressure of small amounts of mixtures (e.g. 10 ml. with constituents having boiling-points differing by 10°). The dimensions of the apparatus are shown in Fig. 22 (II *). The fractionating column is made by indenting spots on a glass tube while hot. The column is surrounded by an evacuated tube which is wound first with asbestos and then with No. 30 chromel wire. This arrangement is used to keep the evacuated space at about 20° below the temperature of the column. This prevents excessive condensation in the column. The flask H is heated by a micro-bunsen burner O. Reflux is provided by the condenser A and can be adjusted by altering the flow of water in the condenser. The rate of condensation is indicated by drops falling back from the tip A₁. The rate of distillation can be observed at E.
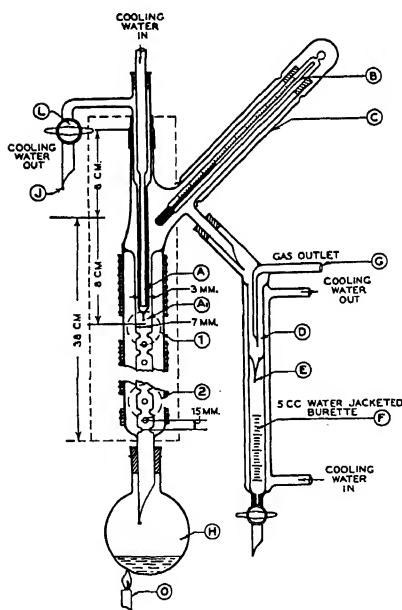
FIG. 22 (II *)

Before distillation the column is warmed up and the apparatus regulated to keep the rate of distillation (about 2–10 drops of liquid per minute)

[1] *Ind. Eng. Chem.*, Anal. Ed., 1934, 6, 323.   [2] *Ibid.*, 29.   [3] *Ibid.*, 235.
[4] *J. Amer. Chem. Soc.*, 1930, 52, 2420.
[5] *Micro-chemie*, 1932, II, 221; also, see Reilly, 'Distillation', *Thorpe's Dict. of Appl. Chem.*, Suppl. 1, 1934, and in new ed. (in press).
[6] *Ind. Eng. Chem.*, 1928, 20, 420.

and the rate of reflux (about 20-40 drops of liquid per minute which can be observed through sighting apertures at 1 and 2) both constant. At the point where one constituent is nearly distilled off a fall in the rate of distillation is observed and additional heat is then necessary for the distillation of the next constituent.

Berl and Althoff [1] describe another micro fractionation apparatus. It is equivalent in its action to a Hempel apparatus, 125 cm. long and employs a fractionating column 40 cm. long and 7 mm. internal diameter. The receiver is water-cooled and terminates in a burette holding 6 ml. and graduated in tenths of a cubic centimetre. The apparatus can be obtained from Firma, M. W. Herbig, Darmstadt, Schlossgartenstrasse, Germany. The micro-analysis of gaseous mixtures by pressure-temperature curves (using liquid nitrogen) is dealt with by Sebastian and Howard.[2] It may be mentioned here that Morton [3] has described a new method for the prevention of bumping in vacuum distillation. It consists of fusing powdered pyrex glass into the bottom of the distillation flask to give a fairly thick coating. The usual stream of air with possible oxidation effects is avoided and the method may be of use in micro work. Other micro distillation apparatus has been described by Fuchs [4] and by Craig.[5]

Solvent Extraction. This refers to the treatment of a mixture with an immiscible solvent (or a mixture of solvents) in which one or more of the components of the mixture are soluble.[6] The extraction process, with Sherwood,[7] is restricted to the separation of the components of a liquid solution by treatment with an immiscible solvent in which one or more of the components of the solution are soluble. This method of separation followed sometimes by fractionation is often more practical than direct distillation (e.g. extraction of dilute acetic acid from an aqueous solution by extraction with toluene, &c.). Sherwood in his book deals thoroughly with solvent extraction. In the proposed supplementary volume of *Physico-Chemical Methods* a separate section will be given to the subject of solvent extraction.

[1] *Chem. Fabrik*, 1930, *3*, 220. [2] *Ind. Eng. Chem.*, Anal. Ed., 1934, *6*, 172.
[3] *Ibid.*, 384. [4] *Microchem.*, 1930, *8*, 159.
[5] *Ind. Eng. Chem.*, Anal. Ed., 1937, *9*, 441 ; see also Ernich Schneider, *Micro-Chemical Laboratory Manual* (New York, 1932).
[6] Reilly and Kelly, *Proc. Roy. Dubl. Soc.*, 1939, *22*, 181, and Reilly, Kelly and Ryan, *J. Soc. Chem. Ind.*, 1937, *56*, 231.
[7] *Absorption and Extraction*, McGraw-Hill, 1937.

SECTION 3: VACUUM DISTILLATION AND FRACTIONATION

Vacuum Distillation.

In addition to lowering the temperature of distillation and prevention of possible decomposition, vacuum fractionation enables mixtures exhibiting only small differences in volatility at ordinary temperatures to be successfully rectified as the volatility differences are found to be increased. Volatility, v, may be defined [1] as the ratio of the equilibrium partial vapour pressure, p, of a component in solution to its mol fraction, c, in the liquid. Relative volatility is then the ratio of the volatility of one component to that of the other. Thus

$$v = p/c$$

If the component obeys Raoult's law in the mixture, $p = Pc$, and it follows that $v = P$, where P is the total vapour pressure. If the component obeys Henry's law, then $p = Kc$, and v at a given temperature is equal to the Henry's law constant, K, at that temperature. It is also possible that mixtures azeotropic under ordinary conditions may not be so under reduced pressure.

FIG. 23 (II *)

Vacuum distillation may be used directly in the purification of compounds, e.g. purification of perchloric acid.[2]

The collection of distillate fractions when distilling under reduced pressure is of some interest. The Bredt and the Gautier receivers are shown in Figs. 23 (II *) and 24 (II *).

Thorpe and Williams [3] describe an interesting modification of the Bruhl receiver. The receivers are mechanically movable and the apparatus is entirely free from glands. The apparatus is illustrated in Fig. 25 (II *). The receivers on the stage of the carrier mechanism may be placed in a bell-jar through one side of which enters the delivery tube of the distillation apparatus, the end of the tube being immediately over the mouths of the receivers.

The following is a description of the apparatus as given by Thorpe and Williams.[4]

The carrier holds twelve glass tubes, A, A, each 2 inches long and $\frac{5}{8}$ inch diameter, and consists of two aluminium discs $3\frac{1}{2}$ inches in diameter separated by
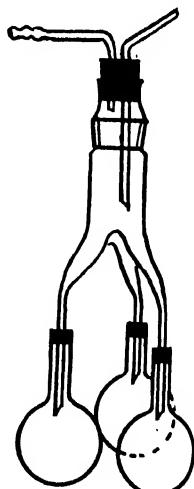

FIG. 24 (II *)

[1] Walker, Lewis and McAdams, *Principles of Chemical Engineering*, McGraw Hill, 1937.

[2] Smith and Goechler, *Ind. Eng. Chem.*, Anal. Ed., 1931, **3**, 48–63.

[3] *J. Sci. Inst.*, 1937, **14**, 178.   [4] *Loc. cit.*

four brass posts $1\frac{1}{4}$ inches long. The top disc B has twelve holes a shade larger than $\frac{5}{8}$ inch in diameter round the edge and a large central hole ; the bottom disc C has twelve corresponding holes $\frac{3}{8}$ inch in diameter and a central hole $\frac{3}{8}$ inch in diameter. This bottom disc is held by screws to a flange D fixed to the hollow spindle E and can be easily removed and replaced by another carrier with a different number of smaller or larger tubes.

This hollow spindle rotates on a cone bearing on the solid post F rising from the base plate, and is lubricated by a drop of 'Hyvac' pump oil.
It carries in addition to the flange D a ratchet wheel G with 48 teeth, and is rotated by the movement of the claw H when the pole-piece K is attracted to the electro-magnets M when current is passed. On cutting off the current the pole-piece springs back to its original position, the claw slipping
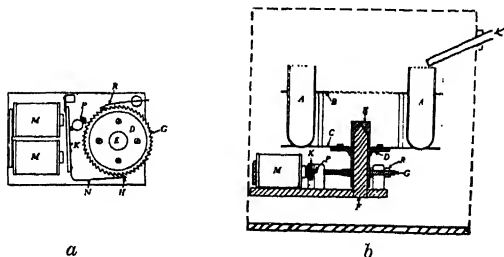
FIG. 25 (II *)

over the teeth of the ratchet wheel, a backward motion of the wheel being prevented by the claw and spring R held in a post mounted on the opposite side of the base plate. The claw H is connected with the pole-piece of the magnets by a light spring N. The movement of the claw is controlled by the adjusting screw P ; overrunning of the carrier is prevented by the tension of the spring attached to claw R. The magnets were adapted from an ordinary electric bell and are connected with a 3-volt battery and a bell-push outside the Bruhl jar. For use with twelve receivers the pole-piece is adjusted by the screw P so that it moves two teeth of the ratchet wheel at a time ; a new receiver, therefore, comes into place by pressing the bell-push twice. The pole-piece can also be adjusted to move three teeth at a time so that a carrier with 8 or 16 tubes can be used. The response to the bell-push is rapid and the designers claim that there is no risk of a drop of distillate falling between the tubes at ordinary rates of distillation. The apparatus has been used successfully at a pressure of 0·1 mm.

Distilling Flask for Reduced Pressures. It is undesirable that any part of a long fractionating column should be borne by a clamp, as it is a heavy piece of apparatus. In distillation under ordinary or increased pressure, ample support is afforded by a stout round-bottomed flask resting on a wire gauze, but it is difficult, if not impossible, to pass the necessary capillary air-tube through a cork or rubber stopper. The double-necked flask D (Fig. 26 (II *)) has been devised to meet this difficulty.[1] The axes of both necks pass through the centre of the bottom of the spherical portion, so that while the fractionating column which is fitted into the wider vertical neck is still supported under its centre of gravity, a capillary air-tube can be inserted through the bent narrow neck with its point in the centre of the bottom of the flask.

Protective Jacket for Thermometers. The thermometer, preferably of the

[1] Wade and Merriman, *J. Chem. Soc.,* 1911, *99*, 984.

Anschutz type, is short enough to be immersed completely in the vapour. It is surrounded by a long narrow jacket J of thin-walled tubing ; and is inserted through the stopper in the position usually occupied by the instrument itself. The bore of the tube is as small as is consistent with the free passage of the thermometer without risk of jamming, and its length is such that the whole of the scale appears below the stopper. Thermal contact is afforded by a small quantity of mercury, which with a little care can be adjusted to reach the level of the bottom of the scale. It is essential that the mercury should be well above the top of the bulb ; the thermometer must therefore be held down in it, preferably by means of a short length of moderately stout platinum wire.

Fractional Separatory Funnels : (a) *Reduced Pressure.* The separatory funnel is free from the common defect of liberating a considerable amount of vapour when the receiver is changed, and also the accumulation of condensed liquid in the connexions and its return at a later stage.

The separator consists essentially of a squat tap-funnel B, into the wide neck of which is sealed a sleeve C, of sufficient calibre to allow the passage of the condenser tube ; the latter, which should project well below the sleeve, is made tight by a short length of stout rubber tubing. The tap P is preferably of large bore—3 or 4 mm. The stem of the tap-funnel is sealed to the upper end of a second sleeve L, the lower end of which carries the rubber stopper of the receiving tube or flask. The two sleeves are respectively furnished with T-tubes TT', the ends of which are sealed to opposite ways of a three-way tap H, the third way of which is open to the air. Connexion with the vacuum pump is made through a branch T'' of the upper side tube.
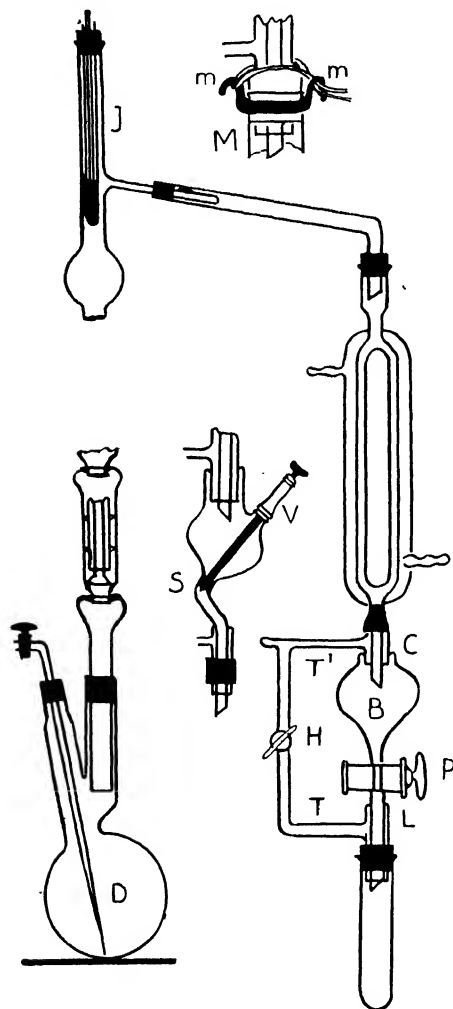
FIG. 26 (II *)

(b) *Increased Pressure.* The tap P of the tap-funnel cannot, as a rule, be lubricated, but as any leakage is inwards no loss is involved. Under

increased pressure, however, a tap is inadmissible, for the leakage is now outwards, whilst the pressure also tends to loosen it. With liquids having no action on vulcanized rubber, a short length of stout pressure tubing provided with a screw-clamp forms an excellent substitute. Where, however, this is inadmissible, the funnel B is provided in lieu of a tap, with an internal stopper S (inset) which can be actuated from outside. The stopper is mounted on a stout glass rod, which passes through a closely fitting glass sleeve V, to which it is secured by a short length of rubber pressure tubing. The tubing, which is wired to the rod and sleeve, acts as a spring, which normally keeps the stopper away from its embouchure in the upper, bent part of the funnel stem. In changing the receiver, the rod is pressed inwards against the elasticity of the rubber tube until it closes the em-
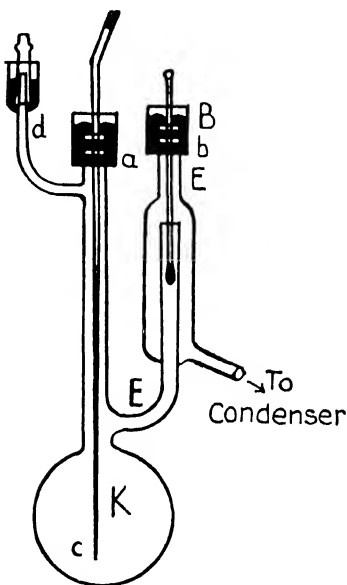
FIG. 27 (II *)
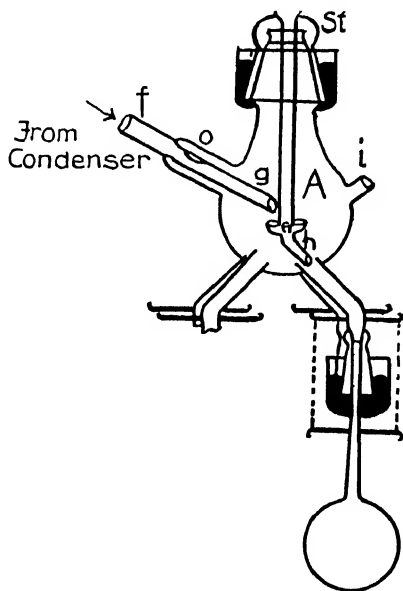
FIG. 28 (II *)

bouchure, and on relieving the pressure by means of the three-way tap, the stopper is held firmly in position by the pressure of the compressed air in the funnel. Any leakage is downwards and internal, and the receiver can be changed so quickly that considerable oozing may take place without loss. In distillation under increased pressure, all the rubber joints and stoppers must be wired to the respective glass vessels and tubes. In fractionation under reduced pressure the frictional hold of the rubber stopper of the receiver is reinforced by the upward pressure of the atmosphere and further support is unnecessary; but with increased pressure the stopper must be secured mechanically. A convenient fastening is afforded by a stout metal ring M (inset), which fits the test-tube fairly closely, and is provided with two stout vertical hooks mm', one of which is radial and the other parallel to the ring; a loop of fairly stout mild steel wire is passed over the first of these hooks, and the two ends, after traversing

the stopper on either side of the sleeve, are sprung under the second, the elasticity of the wire keeping it securely in position.

Kahlbaum's Apparatus. This apparatus, which resembles that of Wade and Merriman, is shown in Fig. 27 (II *). The flask has an attached thermometer-jacket E, a capillary air-tube inlet and an extension d for holding a manometer.

The receiver A can readily be understood by reference to the sectional drawings (Fig. 28 (II *)). The advantages which this receiver offers are ease of manipulation, and the fact that the connexions are made in such a manner that the lower the internal pressure the more securely are they attached. An objection to this apparatus is that all the fractions flow through the same channel h, and consequently each fraction will be contaminated slightly by neighbouring fractions.

Hahn's Apparatus. In the receivers for fractional distillation designed hitherto, the fractions all flow through the same condenser tube, and are separated by altering the relative position of the receiver. As contamination of neighbouring fractions thus occurs, Hahn has designed an apparatus to remedy this defect.

The bulb a', which fits into the neck of the distilling flask a, carries on its upper part three or more side-tubes b, c, d (Fig. 29 (II *)). Into a' fits the hollow stopper e, having a side-tube f, whereby the distilling flask can
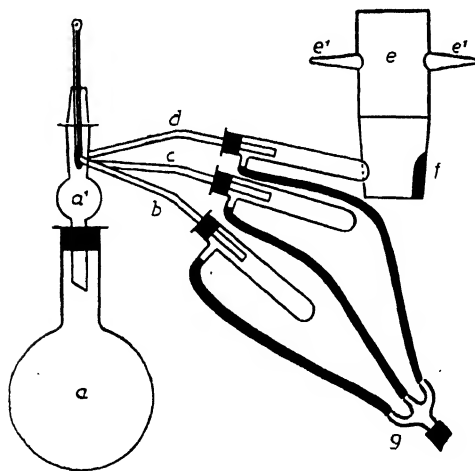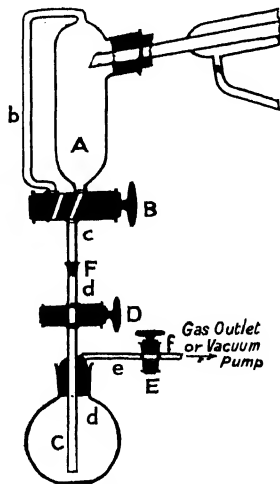
FIG. 29 (II *)   FIG. 30 (II *)

be placed in communication with any one of the tubes b, c or d as desired. The stopper e carries a thermometer and can be rotated easily by means of the projections e', e'. The receivers are connected by means of rubber tubing with the forked tube g, which communicates with the pump. Having collected one fraction by turning e the distilling flask is connected with another condenser, and a screw-clamp is placed upon the rubber tubing between the pump and the receiver containing the fraction.

In Fig. 30 (II *) is shown a convenient form of receiver when distilling in

a current of gas under reduced pressure.[1] The condensing liquid is first collected in A, the three-way tap B being turned so as to connect tubes b and c. The tubes d and e are shown fixed for a heavy gas, e.g. carbon dioxide ; for a light gas the relative depths to which they enter the flask must be reversed.

To isolate the fraction, B is turned to put b in communication with d. The liquid, helped by the gas current, passes into C, B is turned through 180°, and the tube c swept out by gas passing from b. Taps D and E are closed and the ground-glass joint, F, opened. A new flask is put on at the joint, and when the air is removed, the next fractions can be collected. The apparatus may also be used for fractionation *in vacuo.*

Fig. 31 (II *) (private communication from Professor Hilditch) shows the fractionating apparatus which has been employed by the Liverpool school for the fractionation of methyl esters of fatty acids.[2]   Cenco ' Hyvac ' pumps are employed and the working pressure as indicated by a McLeod gauge is usually 0·2 to 0·3 mm.
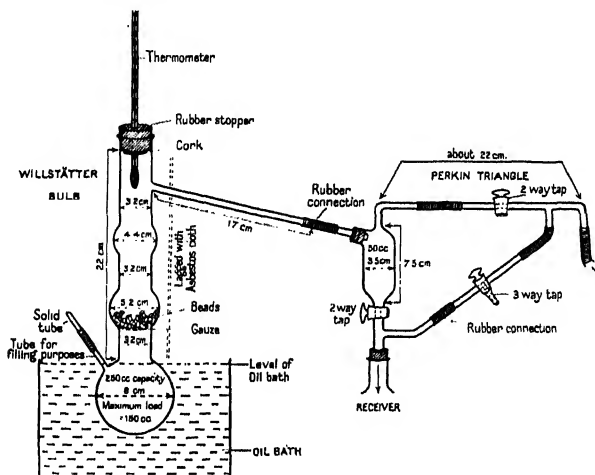
FIG. 31 (II *)

Antifoaming Still-head.[3]

The foaming of liquids when distilled under low pressures (1–2 mm.) is often difficult to control. Eddy[4] describes two forms of still-heads for dealing with this problem. In that shown in Fig. 32 (II *), the foam chamber is vertical and is suitable for solutions having a low surface tension ; the inclined (20° to the horizontal) foam chamber of Fig. 33 (II *) is suitable for solutions of high surface tension. The side-tube A goes to the condenser ; the thermometer being inserted at C. B accommodates a capillary to regulate pressure if necessary. When in operation foam

[1] Wheeler and Blair, *J. Soc. Chem. Ind.,* 1922, XLI, *4,* 59.
[2] See Hilditch and others, *J. Soc. Chem. Ind.,* 1928, *47,* 105T ; 1930, *49,* 363T ; *Biochem. J.,* 1934, *28,* 779, &c.
[3] From Reilly, *Distillation* (Methuen & Co., 1936).
[4] *Ind. Eng. Chem.,* Anal. Ed., 1932, *4,* 2.

passing up the large side arm D must contain enough liquid to carry the foam down the centre tube E, the lower end of which is below the surface of the liquid in the distilling vessel. For experimental purposes the foam chamber can be replaced by an ordinary glass adaptor. Tubes passing through corks replace A, D, and E, the vapour tube D being of larger diameter than the others.

If the amount of foaming is considerable, separation of liquid from foam is even more satisfactory. The high velocity produced by the tube in the foam chamber forces the liquid foam mixture down the centre tube below the surface of the liquid. This reflux action also causes some fractionation. It was found that using this apparatus the time required for distilling foaming liquids was reduced by 25 to 50 per cent.
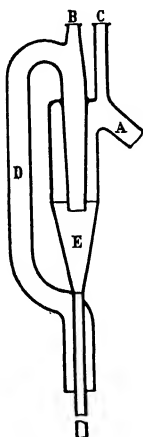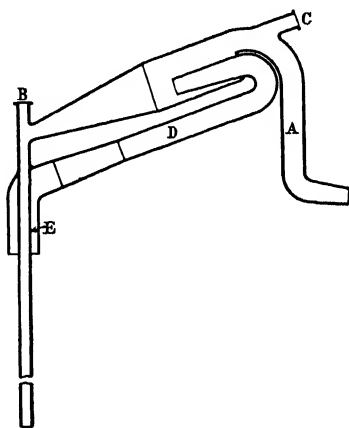
FIG. 32 (II*)   FIG. 33 (II*)

Controlling and Regulating Pressure in Vacuum Distillation. The vacuum necessary for distillation may be maintained by a continually operating pump or by a system in which any increase in pressure over that at which the distillation is to be carried out is automatically dealt with (intermittent pumping system or manostat system). A review of the literature since 1840 on the control of pressure in vacuum distillation is given by Huntress and Hershberg.[1] In general, the intermittent pumping type has distinct advantages. It enables leakage in the evacuated apparatus to be easily detected, as in this event an increase in the frequency of pumping over that intermittently necessary for compensation will be noticed.

Palkin and Nelson [2] have improved on a form of sulphuric acid manostat described by Hershberg and Huntress [3] by elaborating it into an intermittent pumping apparatus. The improved apparatus is very suitable for the setting and maintaining of fixed pressures in conjunction with pressure control devices. In the apparatus two distinct pressure systems are maintained with a different pressure between them of about 4 to 30 mm. The two systems are in intermittent communication with one another by way

[1] *Ind. Eng. Chem.*, Anal. Ed., 1933, *5*, 144.   [2] *Ibid.*, 1934, *6*, 386.
[3] *Ibid.*, 1933, *5*, 344.

of a magnetically operated valve controlled by a Hershberg and Huntress [1] sulphuric acid manostat and thermionic valve relay. In the low-pressure system, pressure is maintained only approximately constant by means of a mercury manostat relay and may be from 4 to 30 mm. lower than the pressure in the distillation system. The flask containing the valve is in direct communication with the distillation system and here the pressure is accurately controlled (see Fig. 34 (II *)).

A small simple magnet with the movable part covered with a strip of smooth rubber is enclosed in the flask F, and constitutes the valve operating mechanism. The movable part of the magnet effects intermittent closure
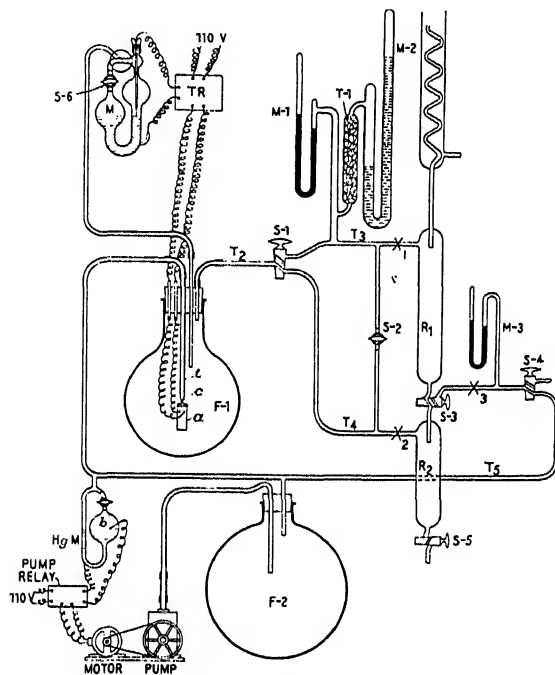
FIG. 34 (II *)

of the capillary opening C at the end of the long 0·125-inch tube t. The sulphuric acid manostat (Hg–M) is similar to the sulphuric acid manostat and is made less sensitive than the usual U-type by making the bulb b relatively larger.

The manometer M–2 is of the U-type and is made from pyrex glass at least 2 cm. inside diameter, to compensate for the high viscosity of the acid.[2] Sulphuric acid (sp. gr. 1·71) as used in the manostat M may be used as the manometer liquid in M–2. After filling, it should be boiled out under a pressure of 1 to 2 mm. of mercury. In this manometer 7·9 mm. of difference in the levels corresponded to 1 mm. pressure of mercury. It is thus nearly eight times as sensitive as the ordinary mercury manometer. The

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[1] *Loc. cit.* [2] *Cf.* Hershberg and Huntress, *loc. cit.*

apparatus is trapped at T_1 with quick-lime to prevent diffusion of gases to or from the acid. Other traps may be used at T_2, T_3, &c.

Flasks F_1 and F_2 are used to eliminate possible pressure fluctuations when the valve opens. Flasks of 5 litres capacity are suitable. The entire apparatus may be made portable (with the possible exception of the pump) and connexions with the distilling apparatus made with rubber tubing at X_1, X_2, and X_3.

The general principle of dual pressure control can also be applied to some advantage even with the pump (mechanical or water aspirator type) continuously operated. If so used the mercury manostat Hg–M and the pump relay are not necessary. Leakage and inadequacy or failure of the condensing system will be indicated by too frequent operation of the thermionic valve relay TR, and of the magnet valve.

For use with a fractionating column the designers recommend the following sequence of manipulation as permitting the taking of fractions during the distillation without disturbing the pressure. To evacuate the system, the manostat stopcock S–6 is opened and the stopcocks S–1, S–3 and S–4 are turned so as to connect F–1 with F–2, and the by-pass between the receivers R_1 and R_2 is opened through S–2, so that the entire system is now connected directly with F–2 and the vacuum pump. When required pressure is reached, S–2 is closed and S–3 is turned on so as to connect R–1 and R–2. At the same time the sulphuric acid manostat is adjusted so that the capillary tip C of the tube t inside F–1 is closed by the rubber pad and the manostat stopcock closed. S–1 is turned on so as to connect F–1 with R–1. Evacuation of F–2 is continued until the desired pressure is reached, as observed on manometers M–1 and M–3, when the mercury manostat Hg–M is adjusted. To remove a fraction of the distillate from the receiver R_2, the designers recommend the following procedure. S–3 is turned to shut off R–1 from R–2 and S–4 is opened to the atmosphere. Through S–3, R–2 is brought to atmospheric pressure and the fraction is run out through S–5. During this operation, the pressure in the distillation apparatus as a whole is being maintained constant. After the fraction has been taken, the pressure R–2 is reduced to that which prevails in the still, in two stages as follows : R_2 is connected with F–2 through S–4 and evacuation continued until the pressure recorded on M_3 has practically reached that of M, and S–4 is promptly turned off. Final adjustment of the pressure in R–2 is accomplished by establishing communication between it and F–1 through S–1, after which all stopcocks are turned to their original position.

Pressure Fractionation

Analogous to vacuum distillation is distillation under increased pressure. Steam distillations are sometimes carried out under increased pressure in order to increase the rate of distillation. Rectification under pressure may be used for substances gaseous under ordinary conditions. Cummings and others,[1] and Brown and others,[2] have given data for rectification of hydrocarbons at high pressures. The production of 99–100 per cent alcohol has also been carried out in a pressure column.

[1] *Ind. Eng. Chem.*, 1931, *23*, 900 ; 1933, *25*, 728.   [2] *Ibid.*, 1932, *24*, 494

SECTION 4 : EVAPORATIVE DISTILLATION

Burch [1] describes an evaporative still for the high vacuum distillation and fractionation of organic substances without decomposition. The still is shown in Fig. 35 (II *). A copper evaporating tray, A (provided with an electric heater in a false bottom), 16 cm. long, 2·5 cm. wide and 1·1 cm. deep, is supported horizontally inside a 4-cm. diameter water-jacketed glass condensing tube, B, which is evacuated by a mercury condensation pump.

The false bottom containing the heater is fixed on to the tray by silver soldering and is connected to the atmosphere by the pipe C, which supports the tray. In this way no vapour molecule can come into contact with the heater element itself. The pipe C, which contains one heater lead and is itself the other, is water-cooled immediately outside the rubber bung at D, through which leads (not shown) are brought out from a thermo-junction
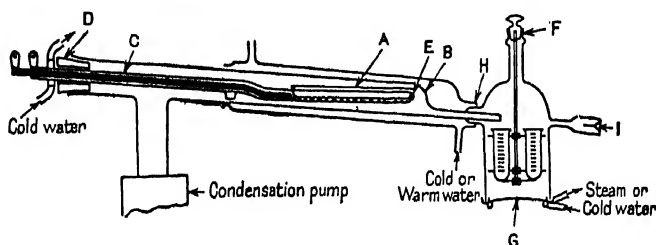
FIG. 35 (II *)

(to measure temperature of distillation) silver-soldered to the tray at E. The lower end of the condensing tube B is sealed into a receiving chamber containing six graduated distillate receiving tubes in a holder which can be rotated by the ground joint F. The bottom of the receiver chamber is closed by a wax joint to a metal plate, G, which can be steam-heated or water-cooled to break or set the joint. The designer found it necessary to seal the condensing tube into the receiver chamber with a re-entrant seal and to arrange the end of the water jacket as shown at H to ensure that the spout inside the receiving chamber would assume as nearly as possible the temperature of the condensing tube. In this way, high melting-point condensates do not set in the spout. An electrode is sealed in at I ; the condensation pump, the evaporating tray and the plate G are connected to earth. In connexion with the degree of vacuum obtainable in the still during the distillations (mostly of petroleum fractions) carried out by Burch [2] an induction coil giving a 1·8 cm. spark between points produced no discharge at the electrode in the receiving chamber (the point of highest permanent gas pressure in the still) during most distillations. During the

[1] *Proc. Roy. Soc.*, A, 1929, *123*, 271.   [2] *Loc.*

distillation of a fuel oil, however, the degree of vacuum obtainable during the earlier stages of the operation was not so high, as the discharge could not be extinguished at the still electrode until a late stage in the distillation. This was due to some rather volatile constituents generally present in fuel oils ; generally speaking, for evaporative distillation preliminary de-gassing by reduced pressure is required for the removal of dissolved gases, e.g. air or carbon dioxide.

In evaporative distillation (i.e. without ebullition) the pressure is so low that the residual gas (e.g. mercury vapour) in the special still has very little influence on the distillation, as the distillate vapour molecules collide more frequently with the walls of the still than with the molecules of residual gas. If a cold condensing surface is placed close to the surface of the evaporating liquid so that a vapour molecule will make no collisions with residual gas molecules or with other vapour molecules during its passage to the condensing surface, then the highest speed of distillation is reached for a given evaporating area : the distilling speed is limited only by the rate of creation of vapour from the liquid and not by the rate of removal of vapour from the vicinity of the liquid.

Furthermore, the density and pressure of the vapour in the diffusing space is very much lower than that of the vapour in equilibrium with its liquid (as in ordinary distillation).

The average distance from the evaporating liquid to the condensing surface is made commensurate with or less than the mean free path of a molecule of distillate vapour in the residual gas (e.g. mercury vapour) at the same density and pressure. In this case practically all of the molecules which leave the surface do not return to it, and this may be termed ' molecular vacuum distillation '. Burch [1] calculates that in the still described above the residual mercury vapour reduces the speed of distillation by about 20 per cent.

For evaporative distillation in the special still it is necessary that the liquid evaporate without the formation of bubbles or splashing. Petroleum fractions (high boiling-point) can easily be evaporatively distilled. Liquids like water, petrol, benzene, acetone and ether exhibit tendencies to foaming under reduced pressure and are almost instantly converted into vapour without rise in temperature. In B.P. No. 303078 (1928) a method is proposed for the evaporative distillation of such liquids in which contamination of the distillate is prevented by baffles.

Burch [1] points out that in ordinary distillation processes (in which ebullition of the liquid is necessary) the vapour immediately above the surface of the liquid being distilled is in equilibrium with the surface layer of liquid at the given density and temperature. The composition of the distillate depends on the temperature alone and not (apart from secondary effects) on the speed of distillation, so that temperature can be adopted as a criterion of composition.

In evaporative distillation, however, temperature is not by itself a criterion of composition, as the speed of distillation must be taken into account. In the case where the evaporating liquid is a chemical individual the rate of evaporation will be $\varrho c/s$ grams per square centimetre per second :

[1] *Loc. cit.*

ϱ is the density of the saturated vapour at the given temperature ; c is the mean molecular velocity and s is the mean free path of a distillate molecule (as above). If the liquid is a mixture the rate of evaporation of the rth constituent will be $\varrho_r c_r/s$, where ϱ_r is the density of the rth component in the vapour and c_r its mean molecular velocity. The separation obtained in ordinary (equilibrant) distillation in which the vapour is in equilibrium with the liquid depends on ϱ_r. In evaporative distillation the separation obtained depends on $\varrho_r c_r$.

c_r is inversely proportional to the square root of the molecular weight and the value of ϱ_r is, in general, greatest for the constituent of least molecular weight, so that $\varrho_r c_r$ is greatest for these constituents. By evaporative distillation an improved separation can, generally speaking, be obtained, e.g. of isotopes. As Burch also points out, it is the only method by which substances of high molecular weight can be distilled without decomposition and it is a method by which it should be possible to avoid constant boiling-point mixtures.

Langmuir's equation for rate of evaporation may be written in the form

$$w = p\sqrt{M/2\pi RT}$$

where M is the molecular weight of the liquid, p its pressure in dynes per cm.^{2} at the absolute temperature, T ; R the gas constant and w the weight of substance evaporating per square centimetre of liquid surface.

Evaporation of a mixture of liquids under non-equilibrium distillation conditions must proceed according to the relation [1]

$$\frac{w_1}{w_2} = \frac{p_1}{p_2}\sqrt{\frac{M_1}{M_2}}$$

where p is now the partial vapour pressure of a component. Sunier [2] points out that for azeotropic mixtures the vapour pressure of the components are usually not equal and that the ratio w_1/w_2 would vary considerably from unity in favourable cases where the ratio of the partial pressures is of the same order as that of the respective molecular weights, so that a decided separation could be expected. In this connexion the design of the 'fractionating alembic' of Hickman [3] should be consulted.

Processes of evaporative distillation have been applied in the separation of the isotopes of mercury and chlorine.

Evaporative distillation has also been employed in the purification of vitamins.[4] In this connexion it is interesting to mention here that the purification of vitamins by fractional distribution in columns between immiscible solvents has been considered in an exhaustive paper by Cornish and others.[5] The process is considered along lines similar to fractional distillation and should be of general application. Fractional distribution

[1] Sunier, *J. Chem. Education*, 1928, **5**, 879 ; *Ind. Eng. Chem.*, Anal. Ed., 1930, **2**, 111 ; Washburn, *Bur. Stand. J. Res.*, 1929, **2**, 476.

[2] *Loc. cit.*

[3] *J. Frank. Inst.*, 1932, *213*, 119.

[4] Carr and Jewell, *Nature*, 1933, *131*, 92 ; British Patent No. 415,088 ; see also Hickman, *Ind. Eng. Chem.*, 1937, **29**, 1107, and Baxter *et al.*, *ibid.*, 1937, **29**, 1112.

[5] *Ind. Eng. Chem.*, 1934, **26**, 397.

can be applied to almost any substance and is not limited to volatile substances as is the case in fractional distillation.

Evaporative fractionation has also been employed by Collins [1] in the fractionation of ethyl esters of fatty acids of high carbon atom content from natural waxes. The apparatus used was similar to that of Bruin.[2] The capacity of the still was 5–6 gm. and it was maintained at constant temperature during the collection of each fraction, thus giving a certain amount of rectification. The pressure was 10^{-6} mm. An iron ball operated by an electromagnet outside the apparatus was used as a stirrer.
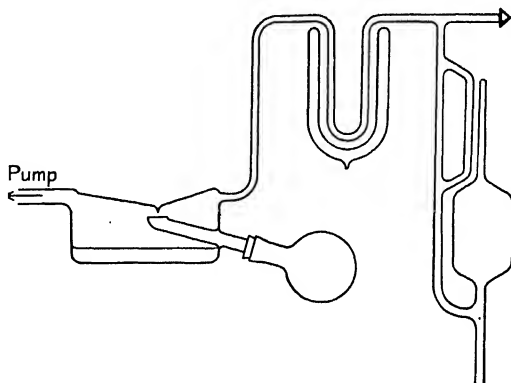
FIG. 36 (II *)

Another high-vacuum evaporative still is described by Hickman.[3] Fig. 36 (II *) shows the design of this still. The vapour is condensed against the roof of the vessel. The floor of the vessel is the still. The McLeod gauge cannot measure the vapour pressure of true evaporative distillation. It will measure, e.g., permanent-gas pressure, e.g. air, during the earlier stages.[4] Under certain conditions the observed rate of distillation will give the vapour pressure, using Langmuir's equation for the amount of substance removed per second per square centimetre of exposed liquid surface (rate of distillation), viz.

$$W = 4{\cdot}374 \times 10^{-5} \times P \sqrt{\frac{M}{T}}$$

W is the weight in grams of a substance of molecular weight M removed per second at P bars (1 bar = 0·00076 mm.) and at temperature T° (absolute). The usual range of pressure is 0·001 mm. to 0·0001 mm.; the rate of distillation practicable in Burch's still is about 20 ml. of liquid per hour.

Nelson and Haller [5] describe two constant temperature baths for molecular stills. The baths are shown in Figs. 37 (II *) and 38 (II *). The still shown in the bath in Fig. 37 (II *) is that due to Mair, Schicktanz, and Rose.[6]

[1] J. Soc. Chem. Ind., 1935, 54, 33T. [2] Bur. Stand. J. Res., 1929, 2, 407.
[3] J. Frank. Inst., 1932, 213, 119. [4] See Hickman, loc. cit.
[5] Ind. Eng. Chem., Anal. Ed., 1937, 9, 402.
[6] J. Res. Nat. Bur. Stand., 1935, 15, 557.

Hickman [1] has developed the concept of the ' elimination curve ' for evaporative distillation purposes, the theory of which is discussed by Embree.[2] Hickman in the former paper also describes a new circulating molecular still which overcomes some disadvantages of the simple pot stills. In the latter preliminary degassing of the material occupies a prolonged period. In addition, the bulk of the material to be distilled is maintained at a high temperature from the beginning of the distillation which may lead to thermal decomposition of the materials to be distilled. Since fractions may be drawn off on incremental increase in the temperature of the heating bath it will be realized that the last fractions will have been in contact with heat from the beginning. Further, since evaporation proceeds from the surface of the liquid, the disposal of the distilland (substance to be distilled) in the form of a film offers advantages.
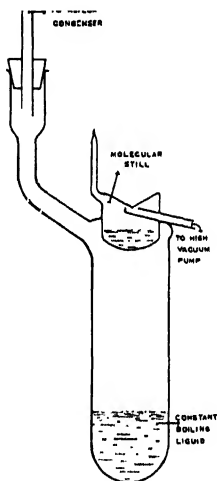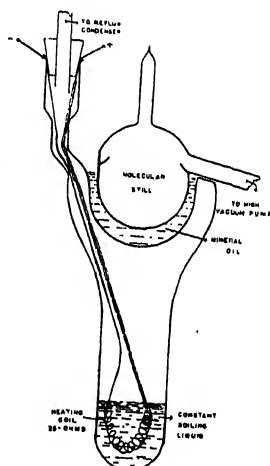
FIG. 37 (II *)   FIG. 38 (II *)

The Hickman circulating still is constructed in two portions. One portion serves to store the liquid at low temperature, whilst the other effects distillation at high temperature. The mass of distilland in the distilling portion is maintained smaller relative to that in the storage part and the total exposure to heat is thus greatly diminished. The substance to be distilled is brought a little at a time from one part of the storage space to the distilling region and then returned to another part of the storage space, so that all portions of the substance may be subjected to degassing and distillation. The distilland is circulated over a heated surface or ' evaporator ', the temperature being raised at each cycle of circulation so that a fraction of distillate may be collected for each circulation. The following description of the apparatus is that given by Hickman.[3]

The apparatus (Fig. 39 (II*)) comprises an evaporator and condenser, A, two reservoirs, C and C', a circulating pump, L, a preheating tube, F, and a withdrawal mechanism, E. Between the evaporating column and the

[1] *Ind. Eng. Chem.*, 1937, *29*, 968.   [2] *Ibid.*, 1937, *29*, 975.   [3] *Loc. cit.*

receivers is a cooling coil, B. To use the apparatus, the liquid to be distilled is placed in the lower reservoir and the vacuum is applied. The liquid is then pumped over the column and allowed to collect in the upper reservoir. The liquid usually froths, and quantities of gas are evolved. When one cycle has been completed, the liquid is transferred to the lower reservoir and a second cycle is performed while the column is warmed. (The liquid may be degassed unattended by allowing it to circulate continuously with the ball displaced from the constriction between the reservoirs.) After a
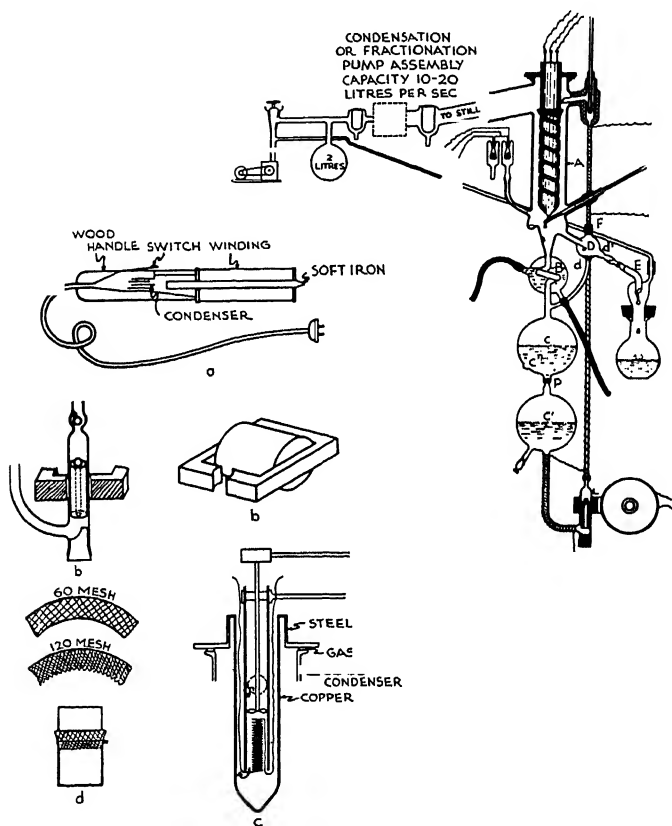
FIG. 39 (II *)

number of cycles, evolution of gas ceases, and when the vacuum gauge records a pressure of less than 2 microns the temperature is raised until condensation takes place on the walls of the receiver. The temperature is held constant until all the distilland has passed over the column. The condensate is removed by changing the receiver, the temperature of the column is increased, and the process is repeated until a sufficient number of fractions has been collected. With a careful disposition of parts, the quantity of material held at the distilling temperatures can be less than one-fiftieth of that maintained at room temperature. Thermal decomposition is reduced fifty-fold, and the quantities of gas to be removed by

the vacuum pumps are diminished in like degree. The average path that a molecule must travel in the distilland to reach the distilling surface is reduced fifty times, and, since the rate of diffusion is an exponential function of thickness, the accessibility of the surface to all molecules is largely increased.

The internal manipulations of the still are controlled by a portable external electromagnet (Fig. 39 (II *) a). Thus, the passage of the liquids is controlled by steel balls (from ball bearings), which are allowed to block constrictions or else rest inactively in depressions in the glassware. The passage of the oil from the upper to the lower reservoir is controlled by the ball P, which can be removed from the constriction between the reservoirs to the position C''. The distillate passes through the filling chamber and drop counter, D, and can pass back to the reservoir or to receiver D. This choice is determined by the position d or d' of the steel ball. It has been found convenient to remove the distillate at atmospheric pressure rather than to use one of the well-known devices which require that a pre-determined number of receivers shall be imprisoned in the apparatus until the end of the experiment. The removal of receivers is accomplished by means of the ball valve between d' and E, and stopcock R. To make the change, the stopcock is closed and the receiver is pulled from its seating, but the distillate is prevented from returning by the ball in F. A new receiver is placed in position, and when the fore vacuum has been re-established, the stopcock is opened and the liquid which has accumulated during the change-over passes into the receiver.

The magnetic circulating pump is made of nickel and glass and is operated by an external electromagnet which receives periodic impulses from a pendulum. The plunger of the pump is made from nickel rod, topped with silver (to hold the ball above the centre of magnetism) and bored with a concentric hole one-eighth inch (3·18 mm.) in diameter. A steel ball rests on the hole at the top of the plunger. A second ball rests on a constriction in the pipe above, and the combination of magnet, hollow plunger, and two ball valves forms the complete pump. Details are shown in Fig. 39 (II *) b. The rate of circulation of the distilland is controlled by raising or lowering the intermittent magnet by a screw adjustment, not shown.

Perhaps the most critical part of the assembly is the distilling column. It should permit the distilland to flow in a thin even stream over the surface. If the fluid gathers into rivulets or channels, the thinner portions will reach the higher temperatures and will distil preferentially, whereas in actual fact the distillation of the thinner streams should be repressed. This causes the constituents of neighbouring fractions to overlap in an unpredictable manner. Unfortunately there is no fixed relation between the temperature of the distilling column and the temperature of the outer surface of the distilland. The two approach one another when the distilland is preheated to the same temperature as the column. The pre-heating operation greatly increases the time during which the substance is held at the higher temperature and is objectionable for this reason only. Where separate preheating is to be used, the column may be made of glass or metal, and a helical electrical heater is sufficiently accurate. It is better,

however, to use the upper portion of the column for preheating the oil. This can be done by increasing the number of turns in the winding of the electrical heater in the upper portion, but it is preferable to use a thin-walled column filled with oil. An electric heating coil is immersed in the oil, and a stirrer circulates the oil rapidly throughout the length. If the column is made of metal of high thermal conductivity, the heat is supplied to the incoming distilland where it is needed without any danger of over-heating. This form of construction is shown in Fig. 39 (II *) c. The column employed for the present work is made of copper, nickel-plated, then chromium-plated and finally burnished to minimize losses by radiation. The distilland is spread on the column by allowing it to fall into two collars of wire gauze, the upper having 60 meshes to the inch and the other 120 meshes. Both strips of gauze are cut from the arcs of circles, and the lower gauze is serrated at the bottom. They are fastened with strands of twisted wire, as shown in Fig. 39 (II *) d. When the distilland stubbornly refuses to spread, a column with a spiral embossing is used. The flanged top of the column rests on gaskets of lead, Duprene, or rubber which make good contact with the ground top of the glass condensing jacket. The column finally adopted had the following characteristics :

Effective length of distilling portion, cm.	15
Diameter, including oil film, cm.	3·7
Approx. distilling area, sq. cm.	170
Total area covered by oil stream, sq. cm. . . .	190
Average quantity of oil occupying working surface, ml. .	4
Average quantity of oil held, ml./sq. cm. . . .	0·0235
Average depth of oil, mm.	0·235
Average time of passage of oil over hot portion of column, sec.	20[1]

[1] The quantity of oil held varies with the rate of flow, the viscosity, and, hence, the temperature. The colder surface layers travel faster than the warm inner layers. More than one-tenth of the oil requires more than 1 minute to travel the 15 cm.

The pressure of residual gas in the still is measured by a Pirani gauge, the setting of which is frequently checked against a master standard gauge. The Pirani gauge is attached to the still at a point farthest from the pump manifold. For producing the vacuum, any condensation pump with a delivery capacity of more than 15 litres per second is suitable. A self-rectifying pump is recommended.

A useful résumé of advances in applications of evaporative distillation is given by Killeffer.[1]

[1] *Ind. Eng. Chem.*, 1937, 29, 966

SECTION 5 : DISTILLATION WITH STEAM [1]

Steam distillation may be divided into two classes, the first comprising distillation at atmospheric pressure—as when a mixture of an organic liquid and water are boiled ; the second, distillation with steam generated independently in a separate vessel and the resulting mixed vapours in each case condensed again to liquid. In the second class, the pressure of the steam has to be reckoned with, especially when this is high.

The distillation of two completely immiscible liquids is represented by the expression

$$\frac{a_1}{a_2} = \frac{p_1 \cdot m_1}{p_2 \cdot m_2}$$

and the mixed vapour will consist of

$\dfrac{m_1 p_1}{p_1 + p_2}$ of the first liquid and $\dfrac{m_2 p_2}{p_1 + p_2}$ of the second liquid, where p_1 and p_2 are the vapour pressures of two liquids at temperature $t°$ respectively.

m_1 and m_2 are their respective molecular weights, and a_1 and a_2 their quantities by weight in the vapour. Thus if the molecular weight of a substance is known and its vapour pressure at the temperature of the distillation, the ratio of the amount of substance that will distil over with the steam to the quantity of water required can be calculated.

Benzaldehyde boils at 178° at ordinary atmospheric pressures. It distils with steam at 97·9°, and this corresponds to its partial pressure of 56·5 mm. The distillate contains 31·4 per cent of benzaldehyde. Again, aniline and water mixture boils at 98·5°. At this temperature, the vapour pressure of aniline is 43 mm. and water 717 mm. The gas law—$PV = RT$ —approximately holds. In the vapour phase we have one volume of aniline at 43 mm. pressure and one volume of water at 717 mm. pressure. The molecular weight of aniline and water are 93 and 18 respectively. Hence the relative proportions by weight of the constituents in the vapour phase are aniline 93×43 and water 717×18 or one part aniline to 3·23 parts of water. This of course assumes that the gas laws hold. On account of mutual solubility, the relative amount of aniline actually found in practice is slightly lower.

In addition to the above application, steam distillation may also be employed to separate the ortho and para phenols, in the separation of arsenic chlorides, to estimate volatile fatty acids and for the separation of many essential oils, and compounds of high molecular weight. These separations are often possible with organic substances having as low as 1 mm. pressure at 100°, especially where the molecular weight is high, e.g.

---

[1] From Reilly, *Distillation*, Chap. VI (Methuen & Co., London, 1936).

a-Santalol boils at 301° and at 100° has a vapour pressure of only 1 mm., yet in steam distillation the distillate contains 0·5 per cent of *a*-Santalol.

Sidgwick[1] states that if two vapour pressure curves are compared it will be generally found that as the temperature rises the ratio of the pressures approaches unity. This follows since the change in vapour pressure with the temperature is given by

$$\log P = A - \frac{B}{T}$$

where A and B are constants determined empirically for each substance, and P is the vapour pressure at the absolute temperature T. If $\log p$ is plotted against $1/T$ for a number of substances, a series of straight lines is obtained radiating from points close together on the $\log p$ axis (where $1/T = 0$ and $\log p = A$). Thus as T rises (i.e. $1/T$ approaches zero) the lines approach one another. It follows, then, that in this region the value of $\log (p_1/p_2)$ approaches zero and $\dfrac{p_1}{p_2}$ consequently approaches unity.

Now since

$$\frac{a_1}{a_2} = \frac{p_1 . m_1}{p_2 . m_2}$$

the efficiency of steam distillation will be greater the higher the temperature or the greater the pressure at which the steam distillation is carried out, i.e. where p_1/p_2 approaches unity. In actual practice it is often convenient to use high-pressure steam in a still which works at a lower pressure than that of the steam. The temperature of the steam is reduced on account of the work done by the steam in expansion against the pressure of the still. To quote but one example of the influence of pressure, it has been shown that the Polenske values of butter rapidly increase with the rise of pressure and can be represented by the equation

$$V = \frac{v(P - K)}{p - K}$$

where V = Polenske value for pressure P
       p = pressure at which the Polenske value is v
       K = a constant or pressure at which Polenske value is zero

Increase in the pressure of steam distillation, generally speaking, increases the rate at which the less volatile substance distils in steam. To take advantage of this many technical steam distillations are carried out under pressure with superheated steam. The influence of electrolytic dissociation on the distillation in steam of certain types of substances has been investigated by Reilly and Hickinbottom.[2] They have worked out an expression to represent electrolytic dissociation and to correct the distillation constant. Correcting for electrolytic dissociation, the distillation constants are practically independent of the concentration within certain wide limits. The addition of salts also in certain cases influences the rate of distillation.

Baker and Pettibone[3] have given a rapid graphical method for the

[1] *J. Chem. Soc.*, 1920, *117*, 396.   [2] *Sci. Proc. R.D.S.*, 1920, XVI, 11, 120.
[3] *Ind. Eng. Chem.*, 1929, *21*, 562.

calculation of steam distillation problems based on Dühring's value. When the temperatures required for steam distillation are plotted against the temperatures at which the vapour pressures of water are equal to the sum of the partial vapour pressures of steam and the substance under distillation, the result is found to be a straight line (Dühring line). The authors give a number of examples of the application of their method.

In Fig. 40 (II *), A is the Dühring line for steam, B for chloroform and C for the steam distillation of chloroform. A and B are obtained in the usual way by plotting the temperature of water exerting a given vapour pressure against the temperature at which the substance exerts the same vapour pressure. A, of course, must necessarily be a straight line. Curve C was obtained as follows: At 30° the vapour pressure of chloroform is 246 mm. while that of water is 31·7 mm., so that the total pressure is 277·7 mm. If 30° is the temperature at which the steam distillation is
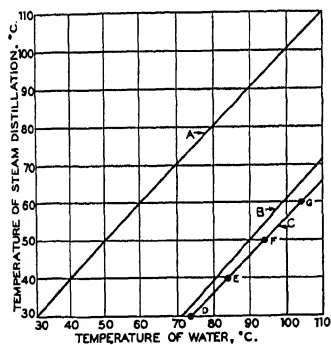
FIG. 40 (II *)
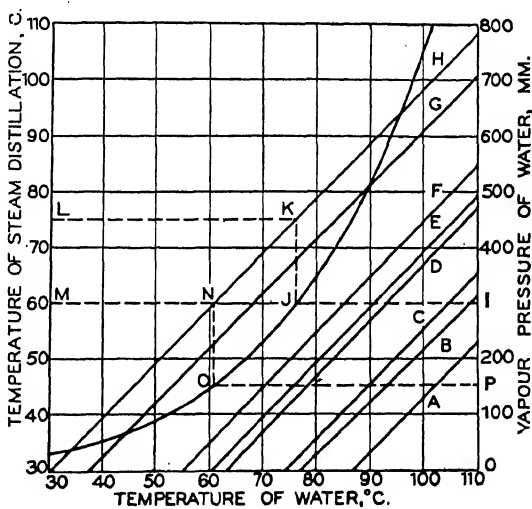
FIG. 41 (II *)

to be carried out, the pressure must therefore be 277·7 mm., which is the vapour pressure of water at 74°. The point D is then plotted with 30° and 74° as co-ordinates. Other points are plotted similarly, e.g. at 60° the vapour pressure of chloroform is 739·6 mm. and that of water 149·2 mm. A vapour pressure of 888·8 mm. (739·6 + 149·2) is exerted by the water at 104·4°. The point G is then plotted with 40° and 104·4° as co-ordinates. These two points would, of course, suffice.

For a given steam distillation temperature, the corresponding temperature at which water has a vapour pressure equal to that necessary for carrying out the distillation can be read from the graph. Knowing this temperature, the pressure of steam may then be read from the tables. This method has been extended to include (*ibid.*) the determination of the temperature of steam distillation when the pressure of distillation is fixed.

In Fig. 41 (II *) there is given the Dühring line for the steam distillation of a number of substances plotted against water as a reference liquid. The

vapour pressure curve of water is also plotted (OV). To find the pressure at which any of the substances may be steam-distilled, at any given temperature, the point on the Dühring line corresponding to the temperature is noted ; one then goes to the vapour pressure curve of water and the pressure so read off. For example, to determine the necessary pressure for the distillation (steam) of aniline at 60° take point M (i.e. 60° being the temperature of distillation) and so arrive at point N, which gives the temperature at which water exerts the same vapour pressure which is given by point O or P, this being 152 mm. When the pressure is fixed the temperature of distillation may be found in a similar way. Thus the line IJKL shows that at 300 mm. total pressure aniline will steam-distil at 75°. The method can also be applied to the steam distillation of complex solutions, e.g. mixtures of hydrocarbons. For details the original paper may be consulted, Baker and Pettibone.[1] Some data are given in Table II.

TABLE II

DATA FOR DISTILLATION WITH SATURATED STEAM

Substance	Slope and Intercepts of Dühring Lines		
	Slope	Intercept on 100° H_2O line	Intercept on 50° H_2O line
(A) Carbon disulphide	0·994	43·2	−6·5
(B) Acetone. . . .	0·972	52·3	3·7
(C) Chloroform . .	0·984	55·6	6·4
(D) Carbon tetrachloride	1·000	67·0	17·0
(E) Benzene . . .	0·992	69·5	19·9
(F) Isopropyl iodide .	0·986	74·7	25·4
(G) Chloro-benzene .	0·968	91·0	42·6
(H) Aniline	0·980	98·6	49·6

A less rapid method for showing the relation between temperatures and pressures in steam distillation involves the plotting of the sum of the vapour pressures of water and the substance being distilled as ordinates against the corresponding temperatures as abscissae. It is assumed that the substance being distilled is immiscible with water at the temperature of distillation and that saturated steam is employed.

A convenient apparatus for carrying out analytical steam distillation is described by Wellman.[2] The apparatus devised by Reilly and Hickinbottom[3] as shown in Fig. 42 (II *) is convenient for distillation at constant volume. The distillation flask is made of quartz, with an inlet tube sealed near the bottom of the flask. The steam jacket consists of a conical-shaped copper vessel with two slots for the passing of the tubes—one at the top to carry the tube leading away the distillation products, and the other at the base, on the opposite side, for the tube leading to the bottom of the flask. The arrangement shown at the side is used for keeping the volume

[1] Loc. cit.   [2] Ind. Eng. Chem., 1931, 3, 281.
[3] Sci. Proc. Roy. Dubl. Soc., 1919, XV, 525.

of liquid in the flask constant. The water is run from a reservoir through a 10-ml. burette, the jet of which leads through a rubber bung fitted with a small tap-funnel. By this means the flow of water can be regulated by two taps, the level of the water in the tap-funnel being kept constant. Reilly and Hickinbottom [1] have used this apparatus to estimate the percentage of butyric acid in butter fat and to determine the distillation constants of lauric and myristic acids. A method of distillation with steam for the quantitative analysis of mixtures of two or three organic substances soluble in water and passing over in steam is given by Reilly and Hickinbottom [2] and by Virtanen and Pulkki [3]; both discuss the enriching effect of salts on the distillate.
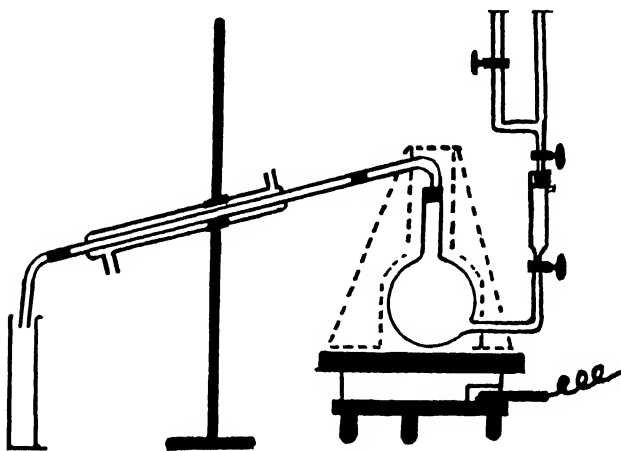
FIG. 42 (II *)

Apparatus for Distillation of Fatty Acids. This apparatus of Reilly and Hickinbottom [4] is shown in Fig. 43 (II *). The flask is surrounded by a steam jacket, the water in which, as well as the contents of the flask, are boiled by the electric heater. To prevent solidification of the acids in the condenser, the leading tube was, as shown, surrounded by an extension from the steam jacket.

Distillation at Constant Volume. *Theory.* The distillation of solutions at constant volume has been studied by Naumann and Müller [5] and by Dyer.[6] A more recent exposition of this subject is contained in the papers of Reilly and Hickinbottom. These authors have formulated a mathematical interpretation of this problem (see original paper).

The Alcohols. Reilly and Hickinbottom [7] have studied the distillation constants of the alcohols and have correlated the mathematical interpretations of former contributors.

[1] *Sci. Proc. Roy. Dubl. Soc.*, 1920, XVI, *12*, 131.   [2] *Loc. cit.*
[3] *J. Amer. Chem. Soc.*, 1928, *50*, 3138.
[4] *Sci. Proc. Roy. Dubl. Soc.*, 1920, XVI, 137. Block of diagram from this paper kindly loaned by Sci. Committee of Royal Dublin Soc. for Fig. 43 (II *).
[5] *Ber.*, 1901, *34*, 224.   [6] *J. Biol. Chem.*, 1917, *28*, 445.
[7] *Sci. Proc. Roy. Dubl. Soc.*, 1921, XVI, 223.
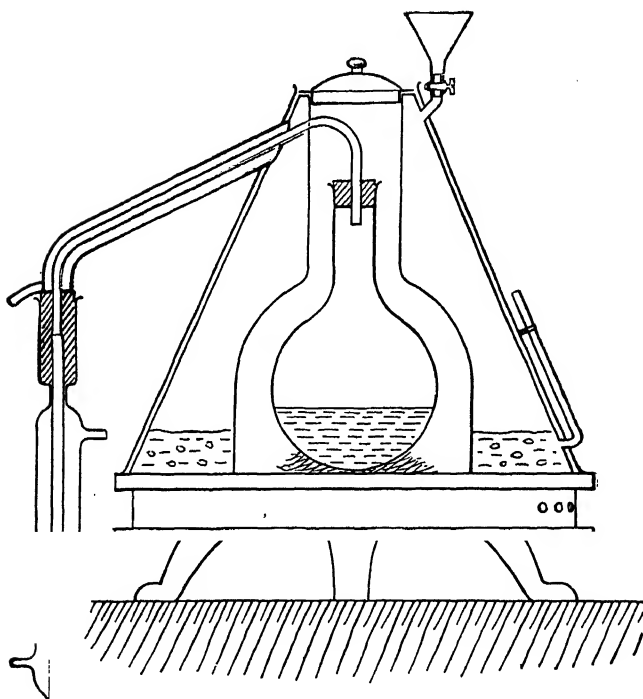
FIG. 43 (II *)

Duclaux's original formula was $\dfrac{da}{db} = c \cdot \dfrac{\_}{a + b}$

where a and b represent the percentage by volume of alcohol and water respectively in the liquid, and da and db the percentage of alcohol and water respectively in the vapour. The above relation may be represented by a hyperbola. The coefficient c increases with the molecular weight of the alcohol. The distillation of dilute solutions can be represented approximately by the expression

$$Va = (V - dV)(a - da) + U \cdot dV$$

$$U = a + V \cdot \frac{da}{dV}$$

where V = volume remaining in the flask at any moment
      a = concentration of alcohol in the solution
      U = concentration of alcohol in the distillate

Mariller uses the coefficient K, which is given by

$$K = \frac{\text{percentage of alcohol in vapour}}{\text{percentage of alcohol in liquid}}$$

or, in the Duclaux notation, $= \dfrac{da}{a} = \dfrac{100c}{ac + 100}$

The coefficient of solution or enrichment K is dependent on the alcoholic concentration.

From the industrial view-point it is important to know the rate at which impurities are removed with respect to ethyl alcohol.

If s be the weight of impurities per kilogram of the original liquid, and S the weight of impurities in 1 kilogram of the mixed vapour, Sorel gives the relationship

$$S = K_1 s + K_2 s^2 + K_3 s^3$$
$$S = K_1 s \text{ approximately}$$

The ratio $\dfrac{\text{percentage of 'impurities' in ethyl alcohol in distillate}}{\text{percentage of 'impurities' in ethyl alcohol in liquid}}$ is

designated K', and it is known as the coefficient of purification.

$$\text{If } k' = \frac{\text{percentage by weight of impurities in vapour}}{\text{percentage by weight of impurities in liquid}}$$

then

$$K' = \frac{k'}{K}$$

The value for K' is largely dependent on the alcoholic concentration of the solution.

The K of Sorel may be expressed in a slightly different form where

a = initial amount of alcohol in flask

x = amount of alcohol in distillate after a volume v has distilled

V = constant volume of liquid in flask

If p = density of water vapour in flask, and σ = weight of water per unit volume of distillate

$$K = \frac{\text{concentration in vapour phase} \times \sigma}{\text{concentration in liquid phase} \times p}$$

$$= k\frac{\sigma}{p} \qquad \lambda = k\frac{\sigma}{p V}$$

$$= \lambda V = A \times V \times 2 \cdot 3026, \text{ where } A = \frac{1}{v} \log \frac{a}{a - x}$$

Method. For the investigation of the distillation constants of the fatty acids, a solution containing at the most 1–2 grams of acid is made up to 200 ml. and distilled in a flask of 300–400 ml. capacity, using an ordinary Liebig condenser. Ten successive fractions are collected; the volume in the distilling flask being kept constant by the addition of water. Each fraction is titrated in turn, so that the acid in all the ten fractions can be determined.

The table on following page gives the results obtained by Reilly and Hickinbottom[1] for acetic acid.

For convenience in tabulating the results $\dfrac{1}{v} \log \dfrac{a}{a - x}$ is multiplied by 10^3.

$\dfrac{p_{n+1} - p_n}{100 - p_n}$ is multiplied by 10^2 and $\dfrac{100 - p_{n+1}}{100 - p_n}$ is multiplied by 10^2.

[1] *Sci. Proc. Roy. Dubl. Soc.*, 1919, XV, 525.

ACETIC ACID

Concentration, 150 ml. of solution require 164·0 ml. of 0·1 N.Ba(OH)$_2$ to neutralize

Weight of fraction in grams.	Titration in ml.	Per-centage distilled	Percent. of 1st 100 ml. distilled over	$\frac{1}{v} \log \frac{a}{a-x}$	$\frac{p_{n+1} - p_n}{100 - p_n}$	$\frac{100 - p_{n+1}}{100 - p_n}$
10	7·65	4·7	12·0	2·07	4·7	0·953
20	7·56	9·3	23·8	2·11	4·8	0·952
30	7·26	13·7	35·2	2·13	4·9	0·952
40	6·94	17·9	46·1	2·15	4·9	0·952
50	6·52	21·9	56·3	2·15	4·9	0·952
60	6·15	25·7	65·9	2·15	4·8	0·952
70	5·98	29·3	75·3	2·15	4·9	0·952
80	5·56	32·7	84·0	2·15	4·8	0·952
90	5·25	35·9	92·2	2·15	4·8	0·952
100	4·96	38·9	100·0	2·14	4·7	0·952

SECTION 6: DESTRUCTIVE DISTILLATION

In connexion with the examination of certain substances it is often necessary to decompose the substance by heat. Where the substance is readily decomposed a glass vessel is sometimes employed.

For the thermal decomposition of petroleum [1] or carbohydrates [2] on a small scale a Jena flask of 300 ml. capacity may be used. To this is fixed a small glass receptacle which is maintained at 60° during the distillation by immersing in a water-bath kept at this temperature. This receptacle is of such a nature that the distillate can be collected in three separate fractions. To this vessel is fitted a large U-tube kept in a mixture of ice and salt so as to retain the volatile products of the distillate in this receiver. The pressure employed during the experiment is maintained between 10 and 15 mm. of mercury. In the initial heating a water pump is sufficient to maintain this pressure, but towards the later stages it is found expedient to employ a Geryk pump. The flask is placed over a heated bath containing a mixture of approximately equal molecular proportions of potassium and sodium nitrates. It is only necessary to immerse the flask in the fusion mixture towards the later stages of the heating, i.e. after about $1\frac{1}{2}$ hours. The temperature of the outside bath varies between 150° and 380°.

For higher temperatures a metal retort may be employed and generally this is heated by gas. For more exact work, e.g. low temperature distillation of fuels, it is more usual to heat directly by an electrical method. It is also possible to effect carbonization by hot gases rather than by direct contact with the heat source. By sweeping off the products of distillation as they are evolved, cracking of the primary tar is prevented.

A retort suitable for such operations is shown.

It consists (Fig. 44 (II *)) of an inner cylindrical container fitting into an outer closed cylindrical jacket, and leaving an annular space of $\frac{1}{2}$ inch between the two. The outer jacket was heated by means of an electrical winding, and gave temperatures up to 650°. This jacket was permanently fixed into a tripod iron casing. The inner container was welded on to a horizontal flange, which could be bolted down to a similar flange welded to the electrically-heated jacket; a gas-tight connexion was made with an asbestos washer between the two flanges; a gas inlet was drilled in the upper flange so that the gas could pass into the annular space between the two cylinders, through the centre cylinder containing the fuel, and emerge through a second aperture drilled in the upper flange. The centre of this flange was drilled and fitted with a closed iron tube for holding a thermocouple, and the inner container fitted with two perforated iron discs, one at the top and one near the bottom. The fuel was kept in position by the perforated discs, the lower one being removed for charging purposes. For

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[1] Reilly, *J. Soc. Chem. Ind.*, 1922, *41*, 302. [2] Reilly, *ibid.*, 1921, *40*, 249.

a distillation a charge of 500 grams of peat was used, the retort being placed in a horizontal position (Fig. 45 (II *)).[1]

The collection of the liquid products resulting from the distillation of either peat or coal is not one of simple condensation, owing to the presence of a 'tar fog'. This fog consists of minute vesicles of gas, which are covered with a film of tar. The surface tension effect of the tar surrounding these particles prevents the tar condensing in the ordinary way. In large-scale practice, condensation of this fog is effected by towers filled with baffle plates or by centrifuging. For small-scale laboratory work these types of precipitators are not generally applicable. During some distillation work which the authors carried out on small samples of coal, it was found that passing the vapours through a column of tightly packed glass wool effectively broke the fog and allowed the tar to condense. An advantage of using this method of trapping the fog was that the tube containing the glass wool could be completely freed from the condensed tar by washing with hot solvent.

FIG. 44 (II *)

The fog or fine particles can be removed also by means of Cottrell precipitators. In these a gas carrying liquid or solid particles in suspension is subjected to a high-voltage (50,000 volts) unidirectional electrostatic field. The suspended particles charged by induction drift towards one or other of suitably arranged poles or electrodes. The gas may also be ionized by having one of the electrodes (in practice this may consist of a wire provided with sharp points inserted in a tube) arranged to have discharge points. The ionized gas drifts towards an electrode and this also helps in the deposition. The high voltage is usually obtained from A.C. current which is stepped up by a special arrangement to give a high voltage of a unidirectional nature.

In carrying out quantitative distillation work it is necessary, for complete extraction of the tar, to use condensing systems which are not complicated. The first condenser was constructed in three sections, consisting of a long-necked (12 inches), round-bottomed flask, a narrow arm leading from the flask in the form of a double U, and a specially constructed fog-trap,

[1] Donnelly, Foot, Nielsen and Reilly, *J. Soc. Chem. Ind.*, 1928, *47*, 1. Donnelly and Reilly, *Sci. Proc. Roy. Dubl. Soc.*, 1930, *19*, 29, 367.

Cool gas from circulating pump
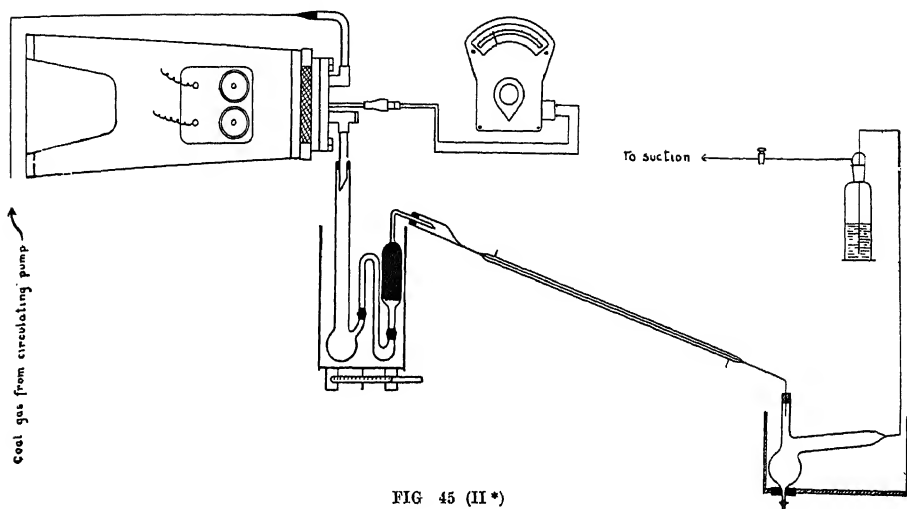
FIG 45 (II *)

tightly packed with glass wool. The three parts were connected in order with wired-on rubber tubing. The first **U** in the lead-off arm from the flask acted as a preliminary baffle for the ' tar fog ', while the second, enlarged to a boat shape, served as a well for condensed tar from the fog-trap. Immersion of this condenser in a bath of calcium chloride solution boiling at 120° ensured that water and oil with boiling points up to 120° were driven over to a second condenser.

The fog-trap consisted of three vertical large-bore glass tubes, connected together at the base and fitted with separate delivery tubes at the top (Fig. 46 (II *)). One of these is seen in the figure, the other two being immediately behind it in the same vertical plane. Any one of the three limbs can be used, the delivery tubes not in use being sealed by insertion in corks fitted into test-tubes.

To enable the tar water to be easily separated from the oil, the second condenser was constructed as a flask-shaped separating funnel, with a wide side arm, 8 inches long, leading from the flask at a slight slope. This condenser was immersed in a freezing mixture of ice and salt at − 20°. In practice it was found that ice was never formed

FIG. 46 (II *)

in the outlet arm at a distance of greater than 3 inches from the flask.
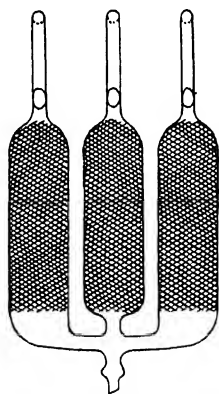
Connecting these two main condensers was a water-jacketed glass tube, $\frac{1}{4}$-inch diameter and 30 inches long, the diameter of the jacket being $\frac{1}{2}$ inch. This condensing tube was necessary on account of the large amount of steam evolved during a peat distillation. On draining the water from the jacket at the end of a distillation, the centre tube was quickly heated by the hot gas from the retort, and any oil that remained was quickly removed.

To overcome the resistance offered by the glass wool to the gas brought

by the circulating pump from the main, suction was applied to the end ⟨ the condensing system. By means of a fine adjustment tap the pressu⟨ in the distillation area was maintained at atmospheric, the tap being opene or closed to the suction as the gas yield increased or decreased.

When starting a distillation one arm of the fog-trap was connected t the second condenser, while the remaining two were sealed. As this ar⟨ became charged with condensed tar (indicated by an increase of pressu⟨ on the gauge) a second arm was used, and the first one sealed. Similarl⟨ as the second arm became charged the third one was used.

The Fuel Research Board [1, 2] have devised a compact apparatus f⟨ this purpose which may be used for the quantitative determination of thes fogs. The principle employed is to raise the velocity of the gas strean locally to a high value and then impose the maximum change in directio⟨
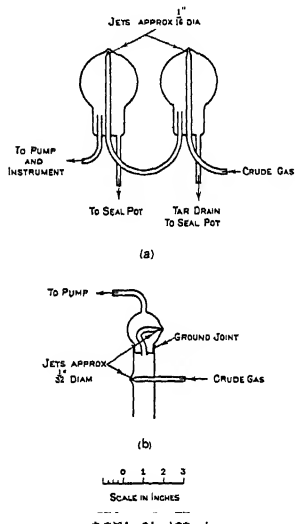
of the velocity by means of an appropriatel⟨ formed surface on which the fog is deposite⟨ The velocity is attained by sucking the ga⟨ stream through a fine jet by means of ⟨ rotary pump. The apparatus is shown i⟨ Fig. 47 (II *). Type (a) will deal with 3⟨ cubic feet of gas per hour. Type (b) will dea⟨ with 10 cubic feet per hour and can be worke⟨ with an ordinary filter pump. The apparatu⟨ can also be adapted to the removal of dust In connexion with the precipitation of fin⟨ dusts in laboratory work, advantage has als⟨ been taken of the method of cloud precipita tion.[3] In this work finely divided product⟨ of combustion of arsenical materials ar⟨ precipitated by a cloud of ammoniun c h l o r i d e. The Gray-King and Lessin⟨ carbonization apparatus are of importance i⟨ the laboratory distillation of coals. These ar⟨ shown in Figs. 48 (II *) and 49 (II *).

The apparatus enables information to be obtained on the amount and nature of the gaseous and liquid products of carbonization. The rate o⟨ evolution of the products at different temperatures may be obtained also ⟨ as well as the effect on the resultant coke of temperature and duration o⟨ carbonization.

For detailed and accurate carbonization data the Gray-King apparatu⟨ (Fig. 48 (II *)) [4] may be employed. The carbonization temperature her⟨ is usually about 600°. The yield of ammonia and coke (including residua⟨ volatile matter) obtained is directly comparable with the yield of large- scale carbonization at the same temperature. The gas and tar yield, however, is usually slightly greater for the laboratory assay. A furthe⟨ advantage is that the cylinder of coke obtained from the laboratory car-

[1] See Reilly, *Distillation* (Methuen), 1936.
[2] *Annual Report*, 1933.
[3] Carey and others, *Ind. Eng. Chem.*, Anal. Ed., 1934, *6*, 327.

bonization is similar to that obtained by large-scale carbonization of the powdered coal at the same temperature.

The apparatus enables the beginning of gas evolution and appearance of oil vapours to be noticed, so that the temperature at which decomposition begins can be recorded. The tar yield is usually sufficient to give a fairly accurate figure for its specific gravity, while the gases obtained may be analysed by the usual methods of gas analysis and the specific gravity also determined.

The retort consists of a hard glass or fused silica tube B approximately 2 cm. diam. and 30 cm. long. It is closed by a rubber stopper. The furnace A is usually a nichrome-wound electric furnace. The temperature is observed by means of a thermocouple, the junction of which is in contact with the outside of the retort tube B in the middle of the furnace. The U-tube C acts as a condenser; the liquid products of carbonization being
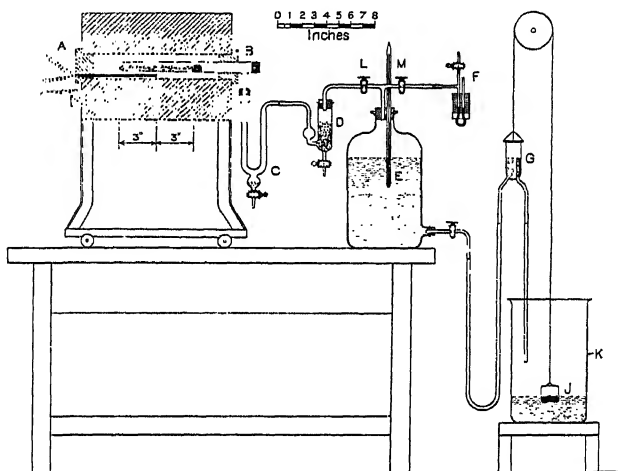
FIG. 48 (II *)

retained in the bulb at its end. The tube D, approximately 2 cm. diam. and 15 cm. long, holds glass beads wetted with sulphuric acid for the absorption of the ammonia formed. The bottle E is a gas holder and is filled with a mixture of equal volumes of glycerine and water. Water nearly saturated with magnesium chloride or with gas from a previous experiment may also be used. A rubber tube connects E to a glass reservoir G. The latter is suspended by a cord passing over a pulley and is counterbalanced by a glass vessel V containing lead shot. During the carbonization gas enters E and so displaces liquid into G from which the excess overflows into the glass tank K in which the counterpoise J floats. E and K are made to have the same diameter so that a fall in the level of the former causes an equal rise of level in the latter. The resulting movement of J causes G to fall by the same amount and so maintain a constant pressure in the gas holder as indicated by F. Before an experiment the height of K or of the pulley may be so arranged that the level in G is below that of the liquid in E so as to give any desired steady difference in level

throughout the test. The connecting tube must be large enough to allow liquid to pass freely from E to G.

For an actual carbonization the coal is powdered to pass through a 60-mesh I.M.M. sieve. It is then dried at 105°–110°, if necessary in an atmosphere of inert gas for coals liable to oxidation.

The gas holder E is filled to the bottom level of the rubber stopper and the reservoir G is adjusted so that the top of the overflow tube to K is approximately 1 cm. below the level of the liquid in E. The tube C is weighed and attached. Approximately 20 gm. of the powdered and dried coal is used for a charge. This is evenly spread out so as to occupy about two-thirds of the diameter of the tube B (previously weighed to the nearest centigram) and is held in place with a loose flattened plug of previously ignited and weighed asbestos wool. The charged tube is then connected by a rubber stopper to C and is given a slight forward slope. The furnace is previously heated to 300° and is then pushed forward into the position as shown in the sketch. When the evolution of expanded air and gas occluded in the coal has ceased, the temperature of the furnace is raised gradually so that the ultimate temperature, 550°–600°, is reached at the end of an hour. During this period the temperatures at which oil appears and at which the evolution of gas begins can be noted. Heating at 550°–600° is continued for one hour ; at the end of this period the evolution of gas falls off and further heating gives only a negligible addition to the volume of gas. At this point the furnace is withdrawn ; the tube B is allowed to cool, the pressure indicated at F is adjusted to zero, the stopcocks L and M are closed and B now opened.

The tube B is weighed when cold to give the yield of coke. After weighing, any tar deposited at the end of B is removed by means of solvents and B is re-weighed. The loss of weight, reckoned as tar, is added to the weight of tar collected in C. The total yield of tar and liquor is obtained from the increase of weight of C. To obtain the separate yields the contents of C are washed with toluene into a 10-ml. graduated cylinder and the volume of the aqueous portion read off. This reading may be converted to grams by taking its specific gravity as unity. Sometimes the meniscus is not clearly defined and it is difficult to read the volume of the aqueous layer. In this case the contents of C from a second carbonization are washed with 50 ml. of toluene into a 100-ml. distillation flask. This is gently distilled until 25 ml. collect in a sutherland burette calibrated for a water-toluene meniscus when the volume of the aqueous portion can be easily read.

The contents of D are washed into a flask and mixed with the aqueous portion from C (from the first test). The mixture is distilled to give the yield of ammonia.

The gas yield remains to be determined. To ascertain the gas volume water is removed from K in a pipette and allowed to flow into G, which is gradually raised until the top of the inlet is level with the liquid in E (the liquid in F being at a level gauge) : any unused water is returned to the tank K. The volume of gas at a definite temperature and pressure (atmospheric) may be calculated from the weight and specific gravity of the liquid in K.

The gas from a first test is usually contaminated with air ; this gas may be used to displace air from the apparatus by driving the contents of E back through the open end of B, leaving the apparatus practically air-free for a second carbonization in which the gas obtained is relatively free from air and may be used for analysis and for the determination of specific gravity. The results obtained may be used to prepare a weight balance of the products. A low-temperature carbonization apparatus to take 500 gm. is described in the Fuel Research Board's paper, No. 21.

The Gray-King apparatus may be adapted to the high-temperature (900°) carbonization assay of coal. This is described in Fuel Res. Board, Tech. Paper No. 24, part III.
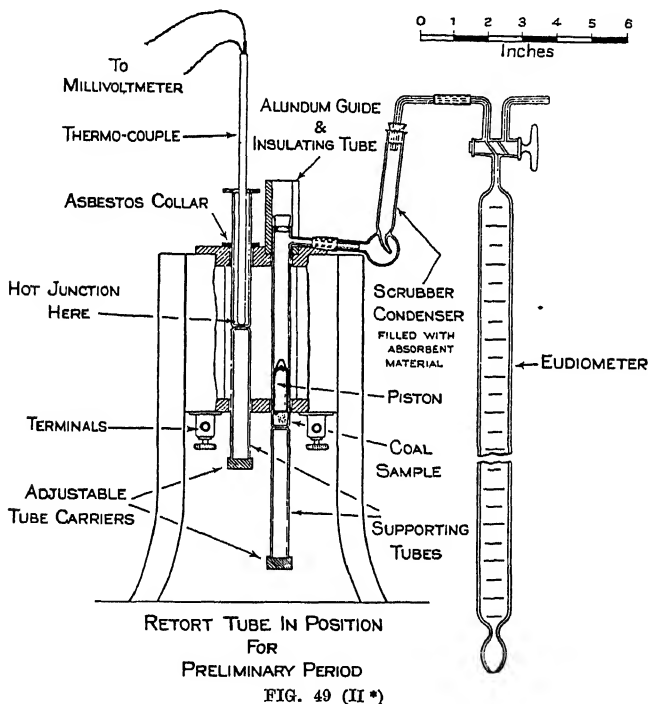
FIG. 49 (II *)

The Lessing apparatus (Fig. 49 (II *)) enables rapid determination of the carbonizing characteristics of a coal to be made under low (600°) or high (900°) temperature conditions. The apparatus enables the physical characteristics of the coke produced at a definite temperature as well as a quantitative estimation of the yields of coke, tar and gas to be determined.

In the apparatus two cylindrical fused silica retort tubes with uniform walls and of definite dimensions are accommodated in an electric furnace. An Alundun tube is used to prevent cooling and subsequent condensation of tar in upper portion of the retort. The apparatus can deal with all classes of coals including highly swelling coals.

During heating a quartz piston fitting loosely in the retort tube compresses the coal, so that only gas and tar vapour, but not coal dust, can pass between

it and the retort wall.   The position of the retort tube can also be adjustec
The tar and liquor are retained in a small glass scrubber filled with cotton
wool, kieselguhr, &c.   The gas volume is read from the eudiometer whic
is provided with a levelling vessel, the filling liquid being a mixture c
equal parts of glycerine and water, &c.   The temperature is obtained b
inserting a thermocouple into the empty retort tube.   Carbonizations a
600° are completed in 15 minutes and at 900° in 7 minutes.[1]

The principles involved in various cracking processes (thermal decom
position), especially for the case of petroleum, are reviewed in *Der Chemie
Ingenieur*.[2]   Modern apparatus and equipment are also described.

[1] See Fuel Research Board, *Methods of Analysis of Coal*.

[2] Edited by Euchen and Jakob.   Revised by Newitt and others.   Vol. 3, *Chemisch
Operationen*, Part 4, *Hochdruckoperationen*, Leipzig, 1939.

SECTION 7 : SUBLIMATION

Conditions for Sublimation. The term sublimation is more especially applied to substances which pass directly from the solid to the vapour state at atmospheric pressure. In practical chemistry, however, substances whose melting-points are high or not far removed from their boiling-points are also included in the category of substances which sublime.

In any event, the condition which determines whether a substance sublimes, or assumes the liquid state before vaporization, is simply that of the pressure at which the change takes place, as a consideration of the diagram (Fig. 50 (II *)) will show. The curve represents the boiling-points of a substance, the curve RX its volatilizing (subliming) points, and the curve XZ its melting-points, under different pressure. The boiling- and subliming-points vary greatly with pressure, the melting-points to so small an extent that the curve XZ is scarcely to be distinguished from a horizontal line parallel with the axis of pressure.

The three curves intersect each other at the point X, which is known as the triple point. At the pressure denoted by this point, and at the corresponding temperature on the axis of temperature, the three phases solid, liquid, and vapour can exist in equilibrium. If the pressure is less than this 'triple point' pressure the substance will pass directly on heating from the solid to the vapour state. The solid cannot melt under these conditions.
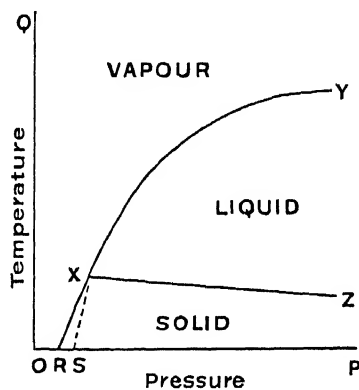
FIG. 50 (II *)

The dotted continuation of the curve X indicates that when the pressure is lowered below the triple-point pressure, a liquid may be cooled below its ordinary freezing-point at atmospheric pressure without solidifying.

The fact that comparatively few substances are known to sublime at ordinary pressures is due to the triple-point pressure being in the great majority of cases far lower than atmospheric pressure. True sublimation can take place only when the partial pressure of the vapour of the substance is lower than the triple-point pressure for the substance. This lowering of the vapour pressure, in the case of substances such as camphor, iodine, sulphur, which sublime in air, is caused by admixture of air with the vapour of the substance. Thus when iodine or sulphur is heated in a retort, while air remains in the vessel, solidification of the element occurs in the neck of the retort. But on continued heating, after all the air has been expelled, the colder parts of the vessel condense the liquid, not the solid, element. The pressure of the vapour has become equal to the external atmospheric

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pressure, is far above the triple-point pressure, and sublimation cannot therefore take place. This is also the explanation of the behaviour of iodine, camphor, and other substances, when heated in an open dish, the fumes of which are caught and condensed on a cold surface. The substance fuses and boils in the dish, where the partial pressure of the heavy vapour alone is higher than the triple-point pressure for the substance, but as the vapour ascends, it becomes so diluted with air that the partial pressure of the vapour falls below the triple-point pressure, and the substance is condensed as a solid.

The heat of sublimation is the sum of the heats of fusion and vaporization at the same temperature. The molecular heat of sublimation is related to the change of sublimation pressure with temperature by the Clausius-Clapeyron equation :

$$H_s = T(V_2 - V_1)dp/dT$$

where H_s = molecular heat of sublimation
T = absolute temp. of sublimation
$V_2 = Mv_2$ (M = mol. wt. of substance ; v_2 = specific vol. of the vapour)
$V_1 = Mv_1$ (v_1 = vol. of the solid)

The relation between heat of sublimation and various optical properties has also been investigated.[1]

Practical Applications. Sublimation processes are used extensively to purify iodine, sulphur, arsenious oxide, ammonium chloride, naphthalene, anthracene, &c. On a large scale the process is used in France, Peru, and Chili for the purification of iodine. The crude iodine recovered from varec or kelp in France, and from the mother-liquors of soda nitrate in South America is heated in earthenware or cast-iron retorts connected to large earthenware receivers. The iodine vapour on entering these wide receivers is largely diluted with air, and its partial pressure soon falls below the triple-point pressure with resultant condensation of the solid.

The sublimation of sulphur, anthracene, arsenious oxide, naphthalene, &c., on the large scale, is similar to that of iodine. In the preparation of arsenious oxide, electrical methods are employed to condense the fine particles of sublimate, which are very liable to be carried away by the vapour of the oxide. Detailed descriptions of the sublimation processes used to purify the above substances will be found in Professor Sydney Young's *Distillation Principles and Processes*.

Laboratory Processes. In the laboratory substances which sublime at atmospheric pressure may often be purified, using the simplest apparatus. Two watch-glasses clipped together with a perforated filter paper between are quite sufficient in the case of an easily volatilized substance. The lower glass contains the substance to be purified ; this is heated. The upper glass is kept cool by moistened filter papers. The sublimate is prevented from falling back into the lower clock-glass by the perforated filter paper. If the substance is difficult to sublime, it may be heated in a crucible inserted in a hole in an asbestos board. The crucible is covered by a large clock-

[1] See Kimura, Sci. Papers, *Inst. Phys. Chem. Research*, Tokyo, 1932, *18*, 157, and *Z. phys. chem.*, 1931, *12*, 717.

glass and surrounded by a filter paper perforated to fit the crucible but not touching it. The sublimate which falls from the clock-glass may be collected on the paper. A small flame is used so that the heat is directed only on to the crucible. Sublimation methods have been used by Reilly and Drumm,[1] and later by McCarthy for the purification of 5-chloro-3-*n*-propyl 1.2.4 triazole.

The purification of dry mercury under reduced pressure, described in the chapter on the Purification of Mercury, is another example of a laboratory process for the purification of a substance by sublimation.

Koehler describes a simple apparatus for the purification of recovered iodine in the laboratory by sublimation. It consists of a glass funnel (Fig. 51 (II *)) in which is placed a tubulated glass globe consisting of halves ground to fit one another, such as is used in vacuum distillations. A glass tube, projecting into the middle of the globe and fitted tightly into the tubulure with asbestos, passes downwards through the stem of the funnel and ends in a glass flask having a hole in the base plugged with cotton wool, and resting on a beaker. The impure iodine is placed in the lower half of the glass globe, and is warmed by a slow current of steam passing through the funnel. A cake of pure dry sublimate is obtained on the upper half, all the moisture passing through the glass tube into the lower flask and beaker. The apparatus works night and day without attention, and using a globe 15 cm. in diameter, 250–300 grams of pure iodine were obtained in a few days.

Even substances of the nature of carbohydrates can be sublimed without decomposition. For example, rhamnose or its hydrate, when heated at 105° at a pressure of 1–2 mm. mercury, sublimes readily, and the sublimate obtained has all the properties of anhydrous rhamnose, and gives the same phenyl osazone. At the same pressure, and at about 100° laevulose also sublimes, but much less rapidly than rhamnose.

FIG. 51 (II *)

Morey describes a convenient apparatus for vacuum sublimation, by an electric heater (Fig. 52 (II *)) specially adapted for the sublimation of large quantities of organic substances.

The apparatus is in use at the American Bureau of Standards, and gives complete satisfaction. It is rapid and efficient, the process is under complete control, and the apparatus requires but little attention. It consists of a large bell-jar (26 cm. diam.) which rests on a glass base plate, the joint between them being well ground, so that with a light film of stopcock grease between the contiguous parts the bell-jar will readily hold a vacuum. A large shallow crystallizing dish which will just sit inside the bell-jar, rests on the glass-plate, and a glass cylinder stands in the dish. This cylinder serves as a support for the electrical heating element, which is of the type ordinarily used in electrically heated hot plates, with an iron
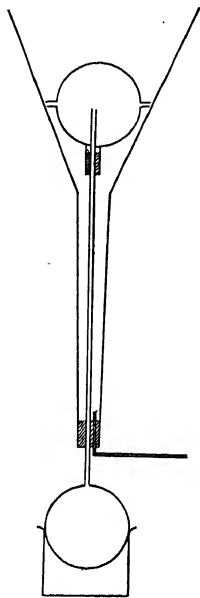
[1] *J. Chem. Soc.*, 1926, 1732.

top and an enamel bottom. The top of the cylinder is loosely ground into the enamel bottom of the hot plate. The glass cylinder also serves to keep the sublimed material from coming in contact with the leads or rubber stoppers through the base plate, and bottom of crystallizing dish. The current wires are led in through the bottom of the dish and pass up through the glass cylinder to the hot plate. The substance to be sublimed is placed in a flat-bottomed platinum dish or crystall-izing dish resting directly on the hot plate. A deep crystallizing dish, with a hole cut out through the bottom to receive the platinum dish, is placed, upturned over the top, as shown, to prevent the sublimed substance coming in con-tact with the hot iron plate. The bell-jar is evacuated through the bottom, the requisite pressure conditions for sublimation being easily obtained. Most of the
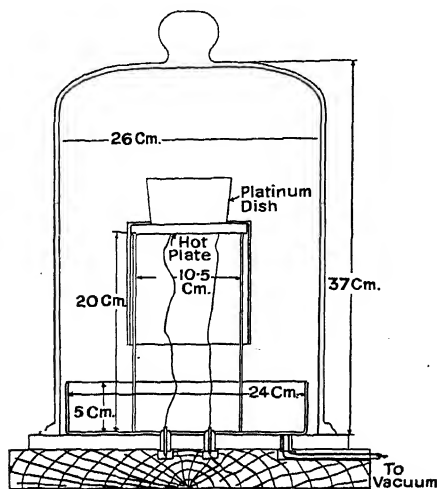
FIG. 52 (II *)

sublimed material drops off from the sides of the bell-jar into the large crystallizing dish. This removal of sublimed material materially affects the speed of the operation, because the solid is not condensed, directly above the unsublimed portion in which case every portion which fell back would have to be resublimed. The apparatus can be readily calibrated so that the approximate temperature can be determined by having an ammeter in the circuit.

Micro-Furnace. What may be described as a useful technique in qualitative and quantitative analysis has been devised by A. L. Fletcher.
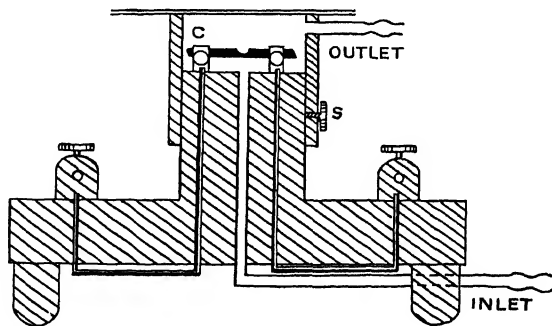
FIG. 53 (II *)

He employs a ' Micro-furnace ' for the sublimation at high temperatures of alloys, minerals, and ores. The micro-furnace, which is shown in section in the diagram (Fig. 53 (II *)), consists of a brass drum sliding over a solid slate cylinder from 5 to 8 cm. in diameter, bearing a pair of terminals for a

carbon rod, which can be heated rapidly to extremely high temperatures by the passage of an electric current.

The sliding cylinder is covered by a receiving-plate of glass, clear or opaque silica, or biscuit ware. The space surrounding the rod can be filled with various gases or rendered partially vacuous by means of inlet and outlet tubes, the former perforating the slate support, whilst the latter is fixed below the upper rim of the brass cylinder. By means of the screw S the size of the chamber and the distance between the carbon and the cover plate can be regulated at will. The inlet tube which opens under the heated carbon tends to transport heavy vapours to the receiving plate.

The substance to be sublimed is placed in a semi-globular depression in the carbon block. Carbon appears to be the best support, because it may be raised to the highest temperature attainable, it prevents oxidation when desirable, and it does not contain impurities likely to affect the analytical results, and does not usually combine with or adhere to the molten metal and hence non-volatile residues may be removed for gravimetric purposes.

As examples of the application of this furnace to qualitative analysis, the following table is presented, showing the colours obtained in air on glass or transparent silica :

| Element.	Deposit.
Copper .	Red, green, yellow
Silver .	Dull grey, pink
Gold .	Red, violet, purple
Chromium	Green
Molybdenum	Pale yellow
Tungsten .	White
Uranium	Black
Selenium .	Red
Manganese	Brown

The colours of the deposit vary with the gas used to fill the chamber. In the presence of hydrogen sulphide, for example, the copper deposit changes from red to greenish black, silver from grey in air to black, cadmium from reddish brown in air to yellow, mercury from greyish white to black. Tin, arsenic, antimony, sublime as white deposits in air, but in H_2S they form respectively black and yellow, red and yellow, and red deposits. The deposit on a plate bearing iodine is in turn distinct from either of the above. Copper is deposited white, silver pale yellow, cadmium white, mercury scarlet and yellow, tin orange brown, arsenic deep yellow, antimony orange red.

From experiments carried out, it appears that the micro-furnace is capable of yielding quantitative results with an accuracy which depends on the nature and relative quantities of the alloy. A quantitative separation, however, can only be carried out in cases where the substances or their compounds with the surrounding atmosphere differ greatly in volatility. In practice a few difficulties arise which may be partly or completely overcome. One constituent of the alloy may be mechanically retained by another, and is thus difficult to volatilize ; thus although tin and lead are to some extent separable, they are difficult to separate completely owing to retention of lead inside the fusion. This is overcome by

alternate heating and cooling, aided by intermediate stirring of the fusion, which brings the lead to the surface.

Another difficulty encountered is the oxidation of the sublimate. When the sublimate oxidizes freely it tends to transport portions of the residue, and this introduces an error into the calculation. This trouble may be combated by using large carbons, or by carrying out the separation in an atmosphere of hydrogen or coal-gas.

The improvement on former methods of quantitative separation by sublimation consists in the fact that the sublimate is not weighed, but estimated by loss in weight of the original amount of alloy taken. The latter, 4 or 5 mg., is placed in the carbon block depression, which is then covered with a fragment of transparent silica. The temperature of the block is then raised slowly until the deposition of one constituent of the alloy is observed on the copper plate. The temperature is then steadied for a short time until this deposition has ceased, when circuit is broken and block cooled. An inspection of the colour and nature of the deposit shows whether the constituent has volatilized pure. To aid this inspection a number of such deposits should first be prepared. This operation is repeated as often as necessary, and the remaining globule weighed. No assumption is made as to the chemical nature and uniform character of the deposit, as would be the case if the sublimate itself were weighed. The micro-furnace thus finds its chief use as a means for ascertaining rapidly what elements are present in any alloy, mineral,- or ore, and roughly in what proportions they are present.

In the simplest form of micro-sublimation for qualitative work, the substance is heated on a microscope slide and condensed on a slide immediately above. If the slide is placed on a heated aluminium block, provided with a thermometer and a glass ring separating the slides, better control can be obtained. In an improved apparatus, continuous cooling by water or air circulation, as well as evacuation of the sublimation space, should be provided. In the apparatus of Clarke and Hermance [1] both the above points are kept in view. The apparatus consists of a cylindrical metal heating block, surmounted by a cooling block of the same diameter. The blocks are maintained in coaxial alignment by a pair of guide rods, over which the upper block slides. A glass ring, ground into grooves in the opposing faces of the blocks, separate them. Water or air circulating through the upper block, cools the glass slip, which receives the sublimate. The sublimation chamber is removable and fits into a plunger mechanism in the heater block. A spring acting against the plunger, forces the chamber up against the cooled glass slip. See original paper for diagrams and working details of the apparatus.

Micro-sublimation in Vacuo.[2] The various methods of micro-vacuum sublimation have been described by Eder and Haas.[3] In Eder's apparatus 10–50 mg. of substance is sufficient at a pressure of 8–12 mm. For larger amounts (0·2 gram) the apparatus of Dupolder [4] is recom-

[1] A New Apparatus for Micro-Sublimation, *Ind. and Eng. Chem. Anal.*, 1939, *11*, 50, reprinted in *Bell's Telephone System. Tech. Publications*, Chemistry, 1939, B, 1122.
    [2] Mitchell, *Recent Advances in Analytical Chemistry*, Vol. II, Churchill, 1931.
    [3] *Mikrochem. Emich-Festschrift*, 1930, 43.
    [4] Houben. *Methoden der Org. Chem.*, 1925, 3rd Ed., Vol. I, 686.

mended. In the paper of Dupolder the characteristic forms of a large number of organic substances are given. Soltys [1] describes two models of a new apparatus in which the vapours pass through sintered glass into the sublimation vessel.

Sublimation of Organic Compounds. Amongst about 5,500 organic compounds (the list of which was taken from Biedermann's *Chemiker Kalender*), over 200 are found to sublime at atmospheric pressure. In the following table a number of the more common of these are given.

Alizarin	Naphthalene
Amino-phenol (Ortho and Para)	Quinone
Anisic Acid	Salicaldehyde (Para)
Anthracene	Salicylic Acid
Anthraquinone	Para Di-Nitro Benzene
Caffein	Phthalimide
Carbanilide	Propionamide
Iodoform	Pyrogallic Acid
Isophthalic Acid	

It is interesting to observe, in the case of di-substituted compounds, that the para compound is generally the one which sublimes, e.g. terephthalic acid, para-amino phenol, para benzoyl benzoic acid, para di-nitro benzene, para salicaldehyde all sublime at atmospheric pressure.

The term sublimation is defined by Hibben [2] in a somewhat different way from the above. He defines it as the process of passing directly from the vapour to the solid state of aggregation and is therefore independent of whether the substance sublimed was originally in the liquid or solid state. He has devised a method of removing dissolved gases from liquids by a process he calls *vacuum sublimation*. Through the application of the method gas-free liquids may be obtained for the determination of physical constants without appreciable loss of either liquid or dissolved gas.

[1] *Mikrochem. Emich-Festschrift*, 1930, 270.

[2] *J. Res. Bur. of Stand.*, 1929, *3*, 97.

CHAPTER III *

MECHANICAL SEPARATIONS[1]

SECTION 1: PHYSICAL ANALYSIS OF SOLIDS

BY physical analysis is meant the segregation of materials according to their physical properties. For example : the iron ore magnetite can be readily separated from associated minerals such as quartz by means of magnetic separation; zinc blende from quartz by flotation, coal may be floated away from heavier minerals upon a suspension of fine sand in water, &c.

It is not proposed to deal here with pseudo-chemical methods of analysis such as those dependent upon differential solubilities; these are dealt with elsewhere.

Some of the methods of physical analysis, and the physical properties upon which they depend, are indicated below :

Size Separation	Size
Classification	{ Size { Specific gravity
Flotation	{ Surface tension of liquids { " Resistance to wetting " or of solids { " Hysteresis of contact-angle "
Magnetic Separation . . .	Magnetic permeability
Photo-electric sorting . .	{ Colour { Lustre
Electrical methods . . .	{ Conductivity { Dielectric constant
Density Separation . . .	Specific gravity

Size Separation. The speed of a chemical reaction involving a solid phase is greatly dependent upon ' dispersion ' of the latter (the greater the surface of the solid exposed per unit volume the more rapid the reaction), and therefore the control of the size of the solid particles plays a very important part in chemical industry.

The methods actually used in any particular process for sizing control depend largely upon the layout of the remainder of the plant as well as upon the grading required. For example, where a process involves very fine and wet grinding, hydraulic classification would be more suitable than screening, but in a dry process screening would be preferable for size separation above 100 mesh and air classification for smaller sizes.

Screens. Screening is the most direct method of sizing and for coarse sizes the most common. For very large sizes of separation grizzlies are

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[1] By C. E. Fenwick of the Cloyne Colloidal Clay Co., Ireland.

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used ; for rather smaller sizes, trommels ; for the finest material shaking or vibrating screens.

Grizzlies consist of parallel bars running in one direction, with cross members for bracing only ; and are used when the size of separation is ½ inch or greater. The grizzly is set at an angle to the horizontal which may be as great as 45°, and the oversize is discharged from the end. Grizzlies are sometimes made with wedge-shaped bars so that the aperture increases from the upper to the lower end of the screen—this construction helps to avoid ' blinding ' or choking. To save head-room grizzlies are sometimes provided with a shaking or rocking mechanism which permits a smaller angle of slope for the same duty ; and occasionally moving chain grizzlies are used.

Trommels are cylindrical rotating screens with their axes slightly inclined and are suitable for rather finer separations than grizzlies. They can also be used for more than one separation size by varying the aperture down the length of the trommel, but such trommels have the objection that all the feed material must pass over the finest screen. Compound trommels, i.e. two or more concentric cylinders with the finest screen outside, are not open to the above objection but repairs are difficult since the outer screens must be removed to obtain access to the inner screens.

FIG. 1 (III *)

Screens must be provided with some form of vibrating mechanism to prevent ' blinding '. Shaking screens are provided with some form of flexible mounting and actuated by an eccentric in a direction parallel to the screen surface. There is considerable advantage in giving the screen a small vertical movement at the end of its forward stroke. Vibrating screens are a development of shaking screens and are set on a small slope and vibrated vertically. One of the well-known types is the Hum-mer, in which the screen wires are drawn up to a considerable tension, and vibrated from the centre by an alternating current electromagnet. The mechanism is illustrated in Fig. 1 (III *).
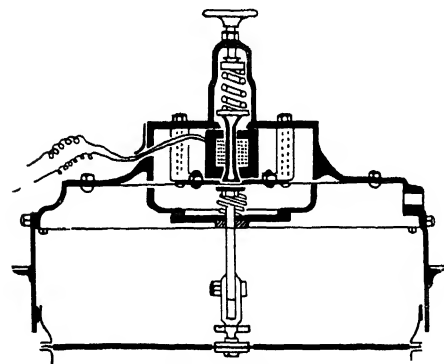
Screen Sizes. Formerly screens were defined by the number of meshes per linear inch, but since the aperture of the screen is dependent upon the wire diameter, such a definition is useless without a knowledge of the latter. Various standard scales have been proposed from time to time, but on account of difficulties in weaving the many odd sizes of mesh and wire, few of them have come into use.

The Committee of Standards of the Institute of Mining and Metallurgy in 1907 adopted a series of screens for Laboratory use (the I.M.M. series). The principal idea seemed to be to use wire the same diameter as the sieve aperture in order to obtain good locking between warp and woof and giving 25 per cent screen opening and 75 per cent dead surface. The

apertures in this series have no fixed ratio, but are always half the reciprocal of the mesh number. These screens are made with extremely heavy wire.

The Hoover series of screens adopted a constant aperture ratio of $\sqrt[3]{2} = 1\cdot2599$, with 1 inch as the standard aperture. This series also contained a screen (the 15th) with an aperture of 1 mm. but it has not come into general use.

The Rittinger series was the first to be proposed and consists of screens having a constant aperture ratio of $\sqrt{2} = 1\cdot414$ starting from 1 mm. aperture.

The Tyler series which has come into common use uses the Rittenger ratio but is based upon a screen which had been already standardized by the U.S. Bureau of Standards, namely, the 200-mesh screen made from 0·0021-inch wire, having an aperture of 0·0029 inch. The aperture ratio being $\sqrt{2}$, the area of the opening in each screen in the series is twice that of the next finer or half that of the next coarser screen.

The following table compares the I.M.M., British Standard Specification, and the Tyler Screen series.

Mesh	Aperture (inches)		
	I.M.M.	Tyler.	B.S.S.
5	0·100	—	0·132
6	—	0·131	0·1107
8	0·062	0·093	—
10	0·050	0·065	0·0660
12	0·042	—	0·0553
14	—	0·046	—
16	0·031	—	0·0395
18	—	—	0·0336
20	0·025	0·033	—
28	—	0·023	—
30	0·017	—	—
35	—	0·0164	—
36	—	—	0·0166
40	0·012	—	—
48	—	0·0116	—
50	0·010	—	—
60	0·0083	—	0·0099
65	—	0·0082	—
70	0·0071	—	—
80	0·0062	—	—
90	0·0055	—	—
100	0·0050	0·0058	0·0066
120	0·0042	—	0·0049
150	0·0033	0·0041	0·0041
200	0·0025	0·0029	0·0030

Classification. Classification is necessary where the the size of separation is too small to permit the use of screens, and is the method of size sorting of particles by their velocities of fall in a fluid. If a mass of grains of various sizes be allowed to settle in a fluid the larger particles fall more

quickly than the smaller, or if the particles be substantially the same size but of different specific gravities, those of the higher specific gravity will fall more quickly.

The velocity of fall is dependent upon the shape, density and size of the particles. Stokes's law of viscous resistance holds where the particles are small and in liquid and the law of turbulent resistance where the particles are relatively large and in a gas. For design purposes a close approximation to the required velocity can be made from these laws and in practice tests are made under plant conditions to determine the exact velocity, which varies with many factors associated with the plant such as the amount of impurity in, and the temperature of, the fluid, the average shape of the particle which varies with the method, grinding, &c.

Hydraulic Classifiers. The simplest form of classifier consists of a launder (or wooden channel) with a series of traps or boxes, which collect different sizes of material. In Fig. 2 (III *) is shown a section of a launder in which the feed enters at A and the liquid moves down the slope with a velocity v and depth d.

If a box X be placed at a distance x from the feed point the time v/x (t) is the period taken for material to travel horizontally from a to x, and
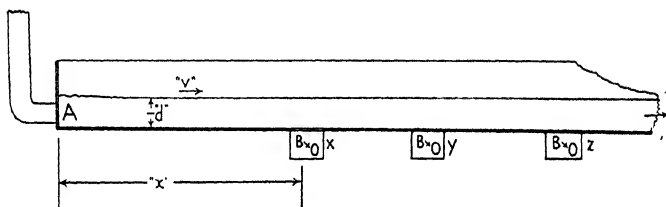
FIG. 2 (III *)

in this time all the particles of solid whose falling velocity exceeds d/t, or dx/v, will have fallen to the bottom of the launder and are being collected in the box. Actually, smaller particles also will be collected from layers below the liquid surface.

Many classifiers have been developed from the elementary type outlined above, and a typical example is the Evans Classifier. In this a supply of fresh water is introduced into the boxes X, Y, Z, &c., part of which flows out through the holes B in the sides, and the remainder flows through the opening into the launder above. The material settling into the boxes is therefore subjected to a rising current of fresh water which prevents finer particles than those desired entering the boxes. Material which is large enough to fall through the rising current is discharged with the water through the holes B. The rising velocity of the fresh water is, of course, progressively decreased from box to box, and the finest material is collected from the end of the launder.

More recent classifiers show great development from the type outlined above. A typical example is the Andrews 'Sy-vor' Classifier; which, shorn of its complexities, is indicated in Fig. 3 (III *). The feed is pumped into a constant head tank A at a rate which maintains an overflow at B and consequently a constant head over the classifier feed jets C. These

jets are arranged tangentially to the cylinder D so that the feed sets up a circular motion in the classifier. The product (fine material) is carried up by the rising liquid, the velocity of which is susceptible to very fine adjustment by varying the syphon head h of the drowned syphon E. Over-size material settles on the internal conical portion and internal baffles (not shown) and slides down to the discharge valve f, receiving on the way a washing with a fresh water-jet, which releases fine material trapped and carried down by the coarser particles. The discharge F may be automatic or manual, but in either case is usually provided with an automatic device which completely shuts it if for any reason the partial vacuum above the liquid surface in D is lost.
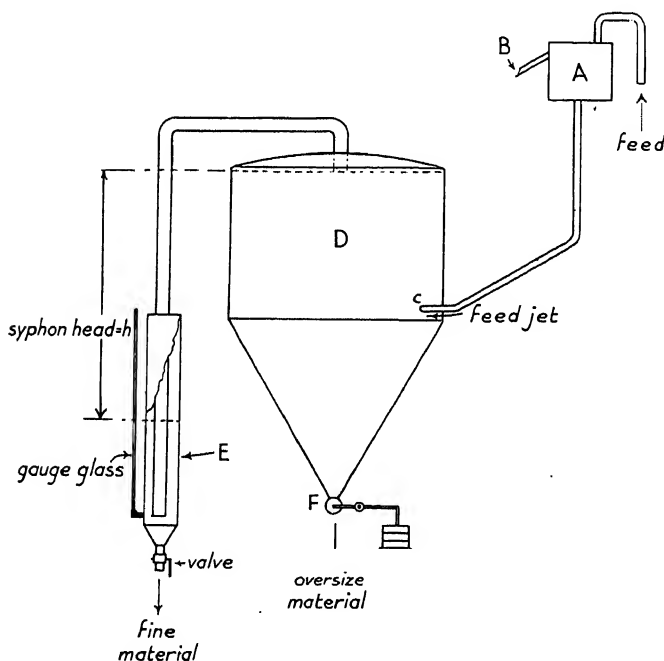
FIG. 3 (III *)

In some classifiers the force due to gravity is replaced or assisted by centrifugal force. An example of this type is the spiral vortex classifier, also due to Andrews. This machine is illustrated in Fig. 4 (III *), in which the feed passage is shown as A, the spiral as B, the over-size discharge as C, and the fines discharge as D. The upper parts of the classifier are a refinement for closer grading. When the classifier starts the coarse material goes out of the tangential oversize discharge c, and the fine material rises through the annular space E and the centre discharge F. The increasing area of the passage E–G, however, slows down the rising velocity and the intermediate particles too large to be carried up by the final overflow velocity collect in the space G and eventually cause a sufficiently high density of liquid here to force practically all the liquid to rise through F. Intermediate material in the centre stream is discarded by centrifugal action

at the change of direction indicated by the arrows **H**.   It will be seen that the overflow is notched ; this is common practice to ensure even discharge round the whole circumference.

Air Classifiers.   Air classifiers may operate on a ' direct lift ' system or on a vortex principle whereby the dust-laden air is whirled round the inner faces of an inverted cone.   As the cone diameter decreases the centrifugal force on the suspended particles increases, and the larger are thrown to the side of the stream where they are free from the air blast, and slide down to the apex ; the fine material is carried on and discharged with the air stream.
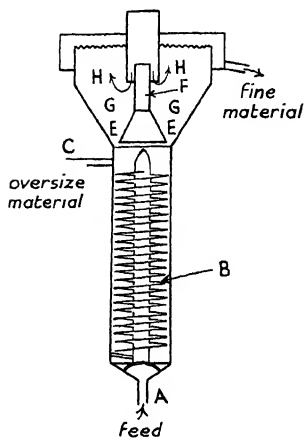
Mechanical Classifiers.   These are desirable where the feed material requires washing to break up aggregations of fine material. One of the best known examples is the Dorr rake classifier, in which reciprocating rakes operate on an inclined bed, the lower part of which dips below the surface of a pond of water.

The rakes are operated by cams and levers, so that they fall, draw material up the sloping bed, rise, return to the back position, fall, and repeat the cycle.   The effect is to withdraw the particles which have settled to the bottom of the pond, stirring them as they are drawn up and keeping the water agitated about the settling material.   Additional water sprays to clean the oversize material may be introduced on the bed above the pond.   The area of the rising overflow column may be varied and thus varying the velocity of the rising current carrying over the fine material.   Separation as fine as 200 mesh may be obtained with this classifier.

FIG. 4 (III *)

SECTION 2: PARTICLE SIZES

Particle size analysis means the separation of a sample of material into fractions of different average diameters. In chemical industries particle size is important on account of the control it exerts on the speed of solid/liquid and solid/gas reactions; and in some, notably the ceramic and cement industries, control of particle size is of extreme importance, as the quality of the final product is dependent thereon.

Sampling. The difficulty of obtaining a sample that is truly representative of the whole bulk of material is not usually appreciated except by laboratory workers. Whatever the material or the form in which it is presented—in piles, in railway trucks, on a conveyor, or as slurry flowing in a launder—the very greatest care must be used when taking samples. If the material is piled, then quantities—say one shovel full—should be taken from all sides of the pile which are accessible, and from different heights. It will be found that the material at the top of the pile contains a much greater proportion of fines than that at the bottom. The shovels so taken should be made into a conical pile, which should be carefully flattened out from the centre outwards and divided into quarters. Opposite quarters are discarded and a new conical pile made from the remaining quarters, taking alternate shovels from each quarter. The shovel must be emptied carefully so that the material runs equally down all sides of the cone. This 'cutting down' process is repeated until a sample of suitable size is obtained. 'Saving time' by shortcircuiting the reducing process always leads to inaccuracy, a fact which is best appreciated from some experience on repeat tests.

If the heaps of material are very wide, or contained in trucks or bins, cores over the whole depth should be taken and mixed. If the material is moving on a conveyor or in a launder, take, if possible, the whole quantity of material delivered for a short time, and if the grading of the material is not uniform with time, take repeat samples at intervals of a few minutes and mix them together.

Crude or careless sampling gives results astonishingly far from the truth; and where possible it is advisable to use mechanical samplers and sample splitters which are independent of any operator's judgement or boredom.

Testing. Hand sieving is the most common method, and in the hands of an experienced operator is satisfactory for separations larger than 200 mesh. The sieves are arranged in a nest, the outer casing of each sieve fitting the casing of the sieve below it, and the nest provided with a top cover and bottom blankpan. The weighed sample is placed on the coarsest sieve, and the whole nest given a preliminary shaking after which each sieve is shaken separately to complete the separation. Both time and intensity of shaking must be kept as uniform as possible. For difficult

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materials or fine sieving a wet method may be used in which the fine material is washed from the coarse particles and through the sieve by a low-pressure water-jet.

A mechanical shaker is preferable to hand shaking since time and intensity of shaking can be exactly repeated from sample to sample. A well-known form is the Ro-Tap shaker, driven by a $\frac{1}{4}$-h.p. motor, which gives the sieves a rotary and tapping motion, similar to the ordinary hand motion.

Size of sample for sieve tests is determined by the characteristics of the material under test. For 10 mesh separation of an easy screening material 200 to 400 grams should be used, for 200 mesh separation 10 to 50 grams. For separations finer than 0·0029 inch (200 mesh on the Tyler series) or at the limit 0·0017 inch (300 mesh) elutriation is used. Elutriation is the separation of material by the action of a rising current of fluid. The process amounts to ' Classification ' with currents of fresh fluid under carefully controlled conditions.

Of the forms of elutriator using liquid the Crooks is the best known instrument, and is illustrated in Fig. 5 (III *). It consists of two cylinders, a lower narrow one A and an upper broad one B. A small movable reservoir C with an overflow funnel and tube D is used to obtain a constant rate of flow upwards for the water. The reservoir C can be moved up and down and constant head and pressure of water may be obtained when these vary in the water-taps. The vessel B is fitted with a double-holed stopper through which passes a straight tube E acting as a manometer and bent tube F with a jet at the end. The velocity of the upward current of water in A and B is regulated by the size of the jet opening and the height of the water level in C; the velocity is indicated by the height to which the water rises in E.

FIG. 5 (III *

The velocity of the rising current required for any size of separation can be calculated by the Schone formula, viz.

$$V = 104 \cdot 7 \ (S - 1)^{1 \cdot 57} \ D^{1 \cdot 57}$$

where

V = mean velocity in millimetres per second
D = mean diameter of particle in millimetres
S = specific gravity of particles

Where very fine separation is required, or where the material is liable to attack by water (e.g. cement) air elutriation may be used. The apparatus must be designed carefully on account of the difficulty of preventing eddies in the air current.

Microscopic sizing analysis is a form of direct counting and is theoretically more accurate than either screening or elutriation. The method is only a guide, however, since the quantity of material visible in the microscope field is very minute, and it is difficult to avoid a large sampling error.
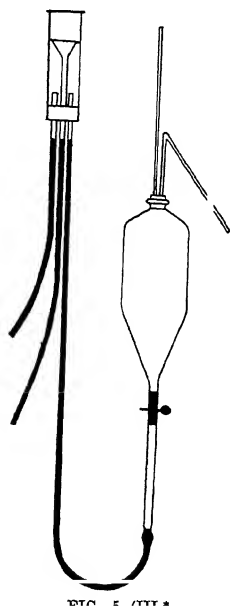
SECTION 3: FLOTATION

The forces which act at a liquid/solid interface are still imperfectly understood, and consequently 'flotation', which depends upon these faces, is still an 'art' rather than an exact science. The processes involved are microscopic and not susceptible to easy examination and include many different factors; it is not surprising, therefore, that flotation has developed on an empirical and experimental basis.

If a drop of liquid is placed upon a solid surface it takes up the form shown in Fig. 6 (III *). The angle COA is known as the angle of contact. The force OB is the surface tension at the solid/gas interface, the force OA is the surface tension at the solid/liquid interface, and OC that at the liquid/gas interface. For equilibrium these three forces must balance and consequently the liquid assumes shape which determines the angle COA. If now the solid be tilted so that the liquid drop runs gently down the inclined plane, the leading angle AOC differs from and is greater than the trailing angle AQY; the former is the maximum angle and the latter the minimum which can be stably maintained by the system of forces. On the generally accepted theory it is the difference between the maximum and the minimum angles of contact rather than the magnitude of the angles which provides the stability necessary to flotation of particles on liquid surfaces. Sulman, to whom much of the flotation theory is due, calls .the difference of the contact-angles the 'hysteresis of contact-angle'.
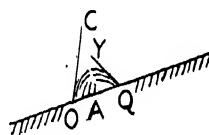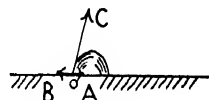
FIG. 6 (III *)

Flotation is of three kinds, which are more or less interrelated; namely, film flotation, oil-buoyancy flotation, and froth flotation. Only the latter is of commercial importance, but chronologically is a development of the two former.

Film flotation is the simplest but is rarely used. The method is to spray very lightly the particles on to the surface of the liquid, skimming the latter to collect those which remain floating.

The oil-buoyancy process is more common than film flotation, but nevertheless has been largely displaced by froth flotation. Oiling particles changes both the contact angle and hysteresis, and when a drop of oil is applied under water to a surface of zinc blende the oil tends to spread and exclude the water from contact with the blende, while on other materials such as quartz the water tends to exclude the oil from contact. The oil buoyancy process, therefore, involves mixing oil with the feed material, preferably under water, in such a fashion that mineral and gangue particles are brought into contact with droplets of oil, then allowing settlement, removing the oil surface containing the mineral.

The third process, that of froth flotation, is of great commercial importance. If particles of galena and quartz are suspended in a liquid saturated with gas, the latter commences to come out of solution and forms bubbles preferentially on the galena particles. Very few bubbles, if any, are formed on the quartz. The tenacity of the bubbles and their preferential formation on the galena is increased by oiling the particles. Solid particles never attach themselves to bubbles already formed—it appears to be essential to the physical process that the gas should form on the solid surfaces direct from the solution.

Froth flotation processes are of two kinds; pulp body and bubble column. These differ both in theory and mechanism.

Pulp body flotation processes may be subdivided into types depending upon how the gas is introduced into the liquid. These include :

Chemical methods, largely used where the raw materials contain calcite or limestone

Electrolytic methods

Pressure reduction methods in which gas already dissolved is encouraged to come out of the solution by a reduction of external pressure

Boiling or heating methods which serve the same purpose

Agitation process, in which a high-speed rotary agitator performs three functions, (a) disperses air in small bubbles throughout the liquid, (b) creates a local pressure on the advancing side of its blades and here dissolves air bubbles, and (c) creates a partial vacuum on the backward side of its blades, here encouraging deposition of the dissolved air.

All the above methods are in common use. In all cases bubbles are formed within the liquid and rise to the surface carrying the mineral particles, forming a layer of froth, from which the mineral is recovered.
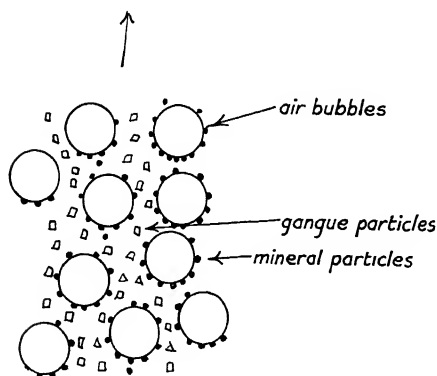
If analyses be made of samples taken from different levels in a pulp body machine, it is found that there is a marked discontinuity in concentration of mineral at the liquid/froth interface. A spot sample of the liquid may show 3 per cent of mineral, while the froth immediately in contact with it may show 30 per cent. In other words, a marked separation takes place at the surface of the liquid.

FIG. 7 (III) *

air bubbles

gangue particles

mineral particles

In the bubble column processes, vastly more gas—usually air—is introduced from externally and the whole depth of pulp converted into a column of froth with an upward movement. The air bubbles are much larger than in the pulp body process and do not firmly retain the mineral particles as the former do. The mechanism of separation is illustrated in Fig. 7 (III *). Both types of particles are falling with respect to the rising bubble column, but the

gangue particles tend to keep to the liquid channels between the air bubbles and have a more or less unimpeded course downwards ; while the mineral particles are attracted to the liquid/gas interface and tend to take a roundabout route downwards, i.e. round the surface of the bubbles. When reaching the bottom of an individual bubble they fall off but are momentarily delayed at each successive fall.

It will be seen that depth analyses such as those outlined for the pulp body process above would show a progressive increase in concentrate from bottom to top, without any marked separation surface. This is the chief difference between pulp body and bubble column processes.

The whole process amounts to a form of classification, the rising current of air or water being replaced by a bubble column and gravity differentiation being assisted by surface tension action.

Flotation plays an exceedingly important part in ore treatment and for more detail, textbooks of Chemistry on Ore Dressing should be consulted.

Magnetic Separation. All substances are to some extent affected by a magnetic field, they are paramagnetic if they are attracted, and are
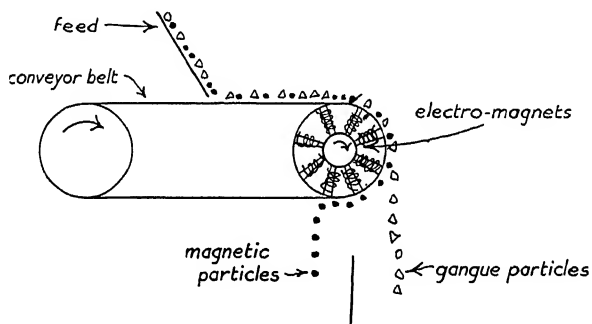
FIG. 8 (III *)

diamagnetic if they are repelled. Strongly magnetic substances are easily separated from weakly magnetic, and weakly magnetic paramagnetic substances can be separated from those which are feebly magnetic or diamagnetic by the use of great field strengths.

Magnetic separators are very common for dealing with either solids or with pulp. The simplest form of separator for solids is the pulley separator, which is illustrated in Fig. 8 (III *). Separators for treatment of liquids can be made on similar principles, but the liquid state makes it possible to use smaller air-gap clearances, and therefore fields of greater strength for the same power input. The liquid is usually passed through or very near a multitude of small gaps in the iron magnetic circuit. This type of separator is especially useful where small quantities of metallic iron have to be removed from large quantities of pulp. Where the magnetic material is the valuable constituent of the pulp continuous machines are used, in which the trapped material is removed during operation. An example of this type is a machine which somewhat resembles a Dorr mechanical classifier provided with a series of magnets under the table. The liquid pulp passes over the overflow leaving the magnetic material to be scraped up by the rakes or screw mechanism.

SECTION 4: OTHER SEPARATIONS

Photoelectric Sorting. Photoelectric sorting is not much used in the field of chemical industry, though it has been proposed and tested for coal sorting. The great improvement of the photo-cell in recent years justifies and will probably increase its application to chemical problems. A black material, such as coal, is carried on a black conveyor belt under a light source and a photoelectric cell is placed so that light reflected from the belt will reach it. If the coal contains lumps of grey shale light is reflected and reaches the cell, which then passes a small current, which, through amplifiers and relays, operates a sorting grab or shovel. A certain amount of light is reflected from the shiny surfaces of the black coal, but false operations from this cause can be prevented by using polarized light and a polarizing screen in front of the cell. It is characteristic of shiny surfaces that they reflect polarized light almost unchanged to which a polarizing screen at right angles to plane of polarization would be impermeable and of matt surfaces that they to some extent ' de-polarize ' light. Separation by colour is possible by screening the light source or the cell to conform with the colour of the material required to trip the circuit.

Photoelectric sorting is necessarily confined to material of fairly large sizes; but in this field of application it may be expected to replace the hand picking now in common use.

Electrical Separation. Low-tension conductivity methods are confined to relatively large feed material as in photoelectric sorting. A plant for sorting bituminous coal has been recently developed in which the mixture of coal and shale is spread on a metallized conveyor belt and drawn underneath a wire brush. Lumps of coal have a lower resistance than shale and when the latter come under the brush, which is kept at a small potential difference relative to the conveyor belt, insufficient current is passed and the circuit balance is upset, operating thermionic relays and a tripping device to eliminate the shale from the stream. If the brushes encounter a metallic vein in either shale or coal, the current passed is so much increased that the circuit balance is again upset and the tripping device is operated.

Extension of low-tension conductivity methods may be expected from the recent development of the gas-filled relay, which makes commercially possible operations so delicate that they are usually classed as laboratory processes.

A high-tension conductivity method is illustrated in Fig. 9 (III *). The electrical brush discharge charges all particles passing over the earthed roller equally, but those which are good conductors rapidly lose their charge to earth, and fall from the edge of the roller. Bad conductors retain their charge, by which they are attracted to the roller, and are carried underneath as shown.

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Electrostatic methods depending upon differences of the dielectric constants of materials have been proposed but are not in use. Electrostatic precipitation of dust from furnace gasses is, however, very common; and is also used in many industrial plants for the recovery of valuable dust.
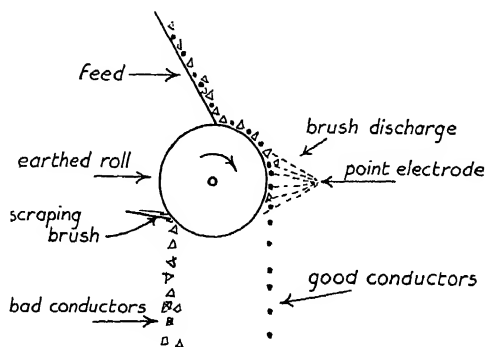
FIG. 9 (III *)

Density Separation. The underlying principle of density separation is simple, but the method is not common in practice though it is used for laboratory purposes. If the specific gravity of the material exceeds that of a liquid it will sink in the latter; if it is less the material will float. Some plants use the method for separating coal from shale, the liquid being a suspension of fine siliceous sand in water; or solutions of calcium chloride may be used to provide a liquid of sufficient density.

CHAPTER IV *

OTHER SEPARATION PROCESSES

SECTION 1: CRYSTALLIZATION

CRYSTAL Habit.—The crystallographic classification of a substance depends on the angle between the faces of the crystal, and is completely independent of the shape and relative size of the faces and the superficial form. The external form which a crystal adopts is governed to a large extent by the conditions under which it is grown. It may be a needle, a prism, or a plate depending on these conditions. Crystal habit bears no relation either to the crystallographic classification or external form of the crystal. The term refers to the relative development of the different types of faces. When sodium chloride is allowed to crystallize from aqueous solutions the faces of the resulting crystal are cubic, whereas if the aqueous solution contains a little urea the crystal faces take the form of octahedra. It will be evident from this that the presence of even traces of impurities in the solvent from which the crystals are separated will often have a very great effect on the crystal habit of the substance. The following descriptions of crystallization and fractional crystallization have been prepared by Miss E. Moynihan.

Crystallization.—Crystallization is a method of purification. The solid product of a chemical reaction is rarely pure. The usual impurities associated with it are unchanged material and by-products. Crystallization is the usual means whereby purification is effected. The impurities are either insoluble in the solvent in which the crystallizable solute is dissolved, and thus are filtered off before crystallization takes place, or they are very soluble and are left behind in the solvent after the crystals have been separated.

Apart from being a means of obtaining substances in a pure condition, crystallization is a process of great importance. The production of crystals, large and well-formed, is an essential step in crystallographic classification.

Crystal Formation. There is very little definite information available on the formation of the crystal nucleus. Many hypotheses have been put forward to explain the established facts, but none seems to be altogether satisfactory.

The miniature crystal, when first it makes its appearance, is called the crystal nucleus. There are many factors influencing the formation of nuclei and the number of nuclei formed. It sometimes happens that a solution is cooled below the temperature at which, under normal conditions, some of the solute should be deposited as crystals. Such a solution is supercooled or supersaturated, and in order to bring about crystallization

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one of the following methods may be employed. (1) The sides of the containing vessel may be scratched with a glass rod ; (2) dust particles may be introduced into the solution, or the solution may be seeded with a crystalline fragment of the crude product.

One of the theories advanced to explain these phenomena was that the fine particles of glass produced by the friction, and the dust particles, &c., served as nuclei on which crystallization could start. The results of later experiments did not confirm this view, and went to show that impact rather than friction is the factor on which crystallization depends. The theory arising from this is that the effect of suspended particles on crystal formation is due to the impacts which take place between the particles.

The number of nuclei formed depends on many things. A solution which is kept absolutely quiet, free from dust and which is of high molecular weight will produce a small number of nuclei, while a large number will be deposited from a solution which is rapidly cooled, stirred vigorously, and is of low molecular weight.

Crystal Growth. When a crystal is suspended in a solution it grows at the expense of the dissolved substance, the solute diffusing to the crystal faces. It may be shown, however, that the rate of growth of the various faces of a single crystal is not the same for all faces. Each face has its own specific rate of growth. The ratio of these rates is constant and, therefore, under constant external conditions a crystal, during the process of growth, retains a fixed geometrical shape.

Size of Crystals. The size of crystals depends on two factors : (1) the number of nuclei formed, (2) the growth of the crystals. It is evident that if nuclear formation is a continuous and rapid process the crystals first formed will have little time to grow, and the result will be a mass of very small crystals. On the other hand, if only a few nuclei are formed at the beginning, and the subsequent precipitation takes' place on these nuclei, the resulting crystals will be large and well formed, but the number will be small. When nuclear formation and crystal growth are simultaneous processes the crystals first formed will eventually be the largest, those last formed will be the smallest, and those formed in between will be of medium size. It is clear, therefore, that the factors influencing nuclear formation will also play a large part in governing the size of the crystal produced.

The Production of Large Single Crystals for Optical Work. It has been shown by Stockbarger [1] that large single crystals of lithium fluoride can be obtained by lowering a pointed-bottom crucible containing the salt through a h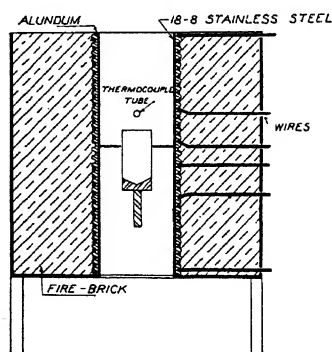igh-temperature gradient region which includes the freezing-point. A diagram of the furnace cross-section used is shown in outline in Fig. 1 (IV *). The

FIG. 1 (IV *)

ALUNDUM   18-8 STAINLESS STEEL
THERMOCOUPLE TUBE
WIRES
FIRE-BRICK

[1] *Rev. Sci. Inst.*, 1936, *7*, 133 ; *cf.* also Walther, *ibid.*, 1937, *8*, 406, on preparation of large single crystals of sodium chloride.

same apparatus has been used again by Stockbarger [1] with modifications of the method to obtain large single crystals of potassium bromide (5 cm. × 5 cm. × 7 cm.) for use in infra-red spectra work. The original should be consulted for details.

Heat of Crystallization.—The process of crystallization is accompanied by an evolution of heat. The heat of crystallization may be defined as the heat evolved when unit weight of a substance crystallizes from a large amount of saturated solution. It is a function of the concentration of the solution.

Methods of Crystallization. Most of the methods employed in the process of crystallization have already been mentioned under 'crystal formation'. The most usual methods adopted are those of cooling and evaporation. In the former the crystallizable substance is brought into solution with heat and the resulting solution allowed to cool rapidly or slowly, with or without agitation, &c., according as the crystals required are to be small or large. If filtration is necessary (the impurities being insoluble in the solvent) it is essential to use a hot filter.

If the crystals do not separate rapidly from the hot solution, and the solution filters rapidly, an ordinary funnel, previously heated, will suffice. If the crystals are rapidly deposited from the hot solution a steam-jacketed or hot water-jacketed filter must be employed. It is advisable to collect the filtrate and to allow the crystallization to take place in a conical flask. When a vessel of this type is used the crystals do not creep up the sides, which so often happens with beakers and test-tubes. After filtration the flask is covered with a watch-glass and the rate of cooling regulated according to the size of crystals required. When crystallization is complete the crystals are separated by filtration and washed with successive small quantities of pure solvent to remove traces of mother-liquor. The crystals are dried by transferring them to a porous plate or pressing them between filter paper.

Crystallization by Evaporation. When the substance is very soluble in all solvents, hot and cold, the method of crystallization by evaporation must be employed. The solution is placed in a crystallizing dish and left in the air or put in a desiccator. It should be remembered that the evaporation should only be partial. If complete evaporation is allowed to take place the fundamental aim of crystallization, which is to effect purification, is not achieved, as the impurities will be left behind with the crystals.

Crystallization by Inoculation. As has already been mentioned, when crystals fail to form due to supercooling the introduction of small crystals of the desired substance has a very stimulating effect on crystallization. This method is called crystallization by 'seeding' or 'inoculation'.

Precipitation by Dilution with a Non-solvent. When crystals fail to separate from solution a very successful means of aiding crystallization is the addition to the solution of a liquid which is completely miscible with the original solvent but in which the solute is insoluble. This liquid, by removing some of the original solvent, concentrates the solution, and crystallization sets in.

Choice of a Solvent. There is a wide range of solvents from which

[1] *J. Opt. Soc. Amer.*, 1937, *27*, 416.

to choose. The ideal solvent is that in which the substance dissolves on heating and is precipitated on cooling, and in which the impurities are either insoluble or very much more soluble than the substance. When making the selection, small quantities of different solvents are added to small quantities of the substance. That solvent in which the substance dissolves on heating and comes out again on cooling, the resulting crystals being large and well formed, is the most satisfactory. It may happen that no single solvent is found suitable. In this case a mixture of two miscible solvents may be employed, in one of which the substance is soluble and in the other insoluble. The substance is dissolved in a small quantity of one solvent and heated, and the second solvent is added to the hot solution until the mixture becomes turbid. The mixture is now heated until complete solution is effected. The solution is then allowed to cool and crystallize. Where the crystalline substance is removed with certain insoluble impurities it is sometimes convenient to separate the soluble portion by means of a soxhlet. A good form of apparatus is shown in Fig. 2 (IV *), in which the risk of breakage of the overflow tube is reduced by being inside the glass container.
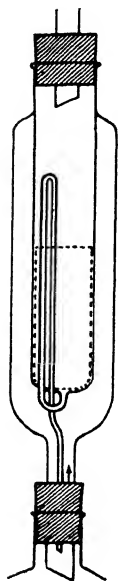
Fractional Crystallization. When it is desired to effect a separation of two or more substances, all of which are soluble in the one solvent, the process of fractional crystalliza-

FIG. 2 (IV *)

tion is employed. Fractional crystallization is based on solubility considerations. It is essential that the substances should have different degrees of solubility, and thus separate at different times from the mother-liquor. Separation is the primary aim of fractional crystallization, but it is also advantageous to get the greatest possible yield of the constituents. With this end in view, many schemes for fractional crystallization have been drawn up.

When a large number of crystal crops is allowed to accumulate, the following scheme may be recommended.[1]

In Fig. 3 (IV *) 1 represents the mixture in solution. On cooling, this solution gives rise to crystals, 2, and mother-liquor, 3. Crystals, 2, are dissolved in as little hot solvent as possible, and the solution on cooling divides into crystals, 4, and mother-liquor, 5. Mother-liquor, 3, is now concentrated and allowed to cool, with the result that crystals, 6, and mother-liquor, 7, are obtained. Mother-liquor, 5, and crystals, 6, are united, and when heated to effect solution and then cooled, yield crystals, 10, and mother-liquor, 11. Crystals, 4, are brought into solution with the minimum quantity of hot solvent, and on cooling divide into crystals, 8, and mother-liquor, 9. Mother-liquor, 7, is concentrated and cooled, and from it crop, 12, and mother-liquor, 13, are obtained. Mother-liquor, 9, and crystals, 10, are united to form one fraction, as are also mother-liquor, 11, and crystals, 12. The operations are indicated in the accompanying diagram, the arrows showing how each fraction is subdivided. When a crop of

[1] Friend, *Textbook of Inorganic Chemistry*, Vol. 4, Griffin, .1928 ; or Cumming, Hopper and Wheeler, *Systematic Organic Chemistry*, 3rd ed. 1938, Constable, London.

crystals is found to be pure there is no necessity to recrystallize it, and its mother-liquor is then treated as already described.
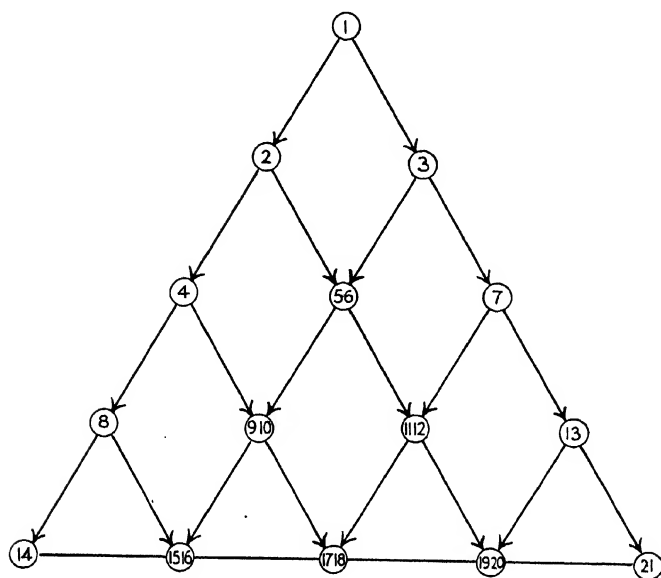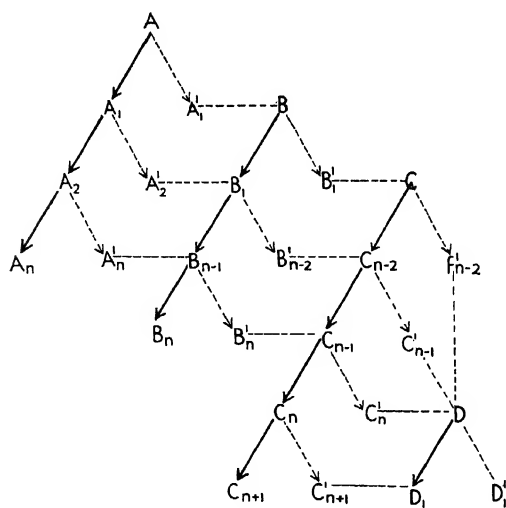

FIG. 3 (IV *)

FIG. 4 (IV *)

When the principal product of a fractional crystallization is fairly soluble in the hot solvent, but only slightly so in the cold, the following

scheme may be employed with advantage. The product is divided into a number of equal portions, A, B, C. A is crystallized from the minimum of hot solvent, yielding crop, A_1, and mother-liquor, A_1' (Fig. 4 (IV *)). Mother-liquor A_1' (and the washing from A_1) serve to crystallize B to give crop B_1 and mother-liquor B_1'. Mother-liquor B_1' is in its turn used to crystallize C. Mother-liquor C_1' should be almost saturated with the impurities, while it contains very little more of the principal product than was present in mother-liquor A_1'. If crop A_1 is not pure it is recrystallized, using pure solvent, and crop A_2 and mother-liquor A_2' are obtained. Mother-liquor A_2' is used to crystallize B_1, and mother-liquor B_2' to crystallize C_1, and mother-liquors C_1' and C_2' are united. The process is continued until A is pure. The B crop then becomes the first fraction, and mother-liquors C_1', C_2', C_3', &c., are united and evaporated to yield crop D, which now becomes the end fraction and takes part in the crystallization process.

Rate of Crystallization. Michel [1] made a study of the rate of crystallization of a large number of organic compounds as a criterion of purity of the substances. Various degrees of undercooling were employed and containers of varying dimensions also used. The apparatus consisted of an insulated glass tank 20 litres capacity. Dewar flasks were used for experiments at very low temperatures. He concluded that the rate of crystallization can serve as a criterion for both identity and purity of a compound—the more symmetrical derivatives have the higher rates of crystallization. The inside diameter of the capillary tubes does not affect the maximum rate of crystallization. The thickness of the walls of the tube influences the formation of spontaneous crystals. Ultrafiltration increases the tendency towards undercooling but does not affect the rate of crystallization. The results were reproducible.

[1] Methods and Apparatus in use at the Bureau of Physicochemical Standards, Part X, *Bull. Soc. Chim. Belg.*, 1939, *48*, 105, 57.

SECTION 2 : CENTRIFUGAL ACTION

As a means of separating (i) two liquids of different densities forming an emulsion, (ii) the suspended material in a colloidal solution, (iii) sediments, (iv) fine precipitates, &c., the use of a centrifuge is advised. It is also useful in securing clear filtrates from very fine precipitates or in obtaining clear aqueous extracts from soils. The principle of the separation depends mainly on three factors :

(a) The difference in the densities of the two constituents.

(b) The temperature—on which depends the viscosity of the liquid about to be centrifuged.

(c) The radius of the suspended particles (in case of emulsoids and suspensoids).

The centrifugal force on each particle causes the heavier material to sink to the bottom of the container and as the velocity of revolution is very great (2,000 to 40,000 r.p.m.), the constituents are usually completely separated in 3 to 4 minutes. The constituents are then easily obtained by decantation through a filter. In the case of suspended particles the supernatant liquid can be decanted off quite easily. In cases where other special filters do not separate fine suspensoids the method of centrifuging has been found to work quite satisfactorily.

For research and general laboratory use the different centrifuges may be divided into three types, namely the hand-driven centrifuge, the electric centrifuge and the supercentrifuge.

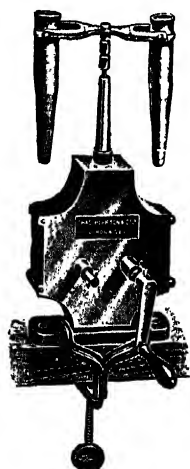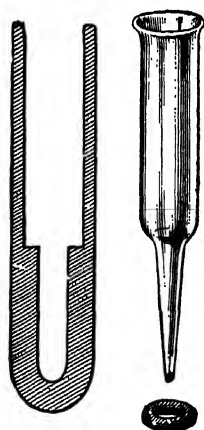**Hand-driven Centrifuge.** The centrifuge is enclosed in a protective

FIG. 5 (IV *)   FIG. 6 (IV *)

case and bolted securely or clamped on a firm bench so as to secure an accurate balance. Fig. 5 (IV *) shows a simple form of such an apparatus.

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The centrifuge tubes which are arranged diametrically opposite are enclosed in aluminium tube holders. Each tube is marked for a capacity of 15 ml. of the fluid and one is graduated into 150 parts, permitting quick readings of the precipitates. The tubes which are vertical while the centrifuge is stationary are then filled to the mark with the liquid. While it is not necessary to fill all the tubes, care must be taken to fill the diametrically opposite tube in each case as equality of weight is essential for equilibrium. The number of tubes usually varies from 2 to 32 and while 15 ml. is the usual capacity, sometimes tubes of 20 to 25 ml. are used. Fig. 6 (IV *) is that of the 10 ml. pointed tube with its adaptor as used in the above centrifuge. The disc is rotated by means of a handle and the tubes or buckets, as they are called, being free to rotate, assume a horizontal position as the velocity increases. The velocity usually varies from 2,000 to 3,000 r.p.m. After a short time, on slowing up the centrifuge it will be found that the solid material (if denser than the liquid) has fallen to the bottom of the tubes which have again swung into the vertical position and it can readily be recovered by decantation. For revolutions more than 2,000 per minute a protecting cover or guard is advisable. This method of separation is very useful in the examination of milk, water, blood, urine, sputum, &c.

The Mechanically-driven Centrifuge. This centrifuge is constructed on a low substantial base (cement) so as to ensure smooth steady running. It usually contains 6 to 8 tubes which are generally made of fairly thick glass and conical in shape. These are of the capacity of 50 ml. or 100 ml. and are enclosed in brass buckets. As in the case of the hand centrifuge they are situated diametrically opposite and occupy a vertical position while at rest, but revolve into a horizontal position on rotation. Whatever tubes are used should be filled with an equal volume of liquid and a symmetrical distribution of the liquid be made. In this way an evenly distributed load about the axis is secured. The whole centrifuge is enclosed in a strong protective cover with lid and has attached a speedometer (Fig. 7 (IV *)). A belt leads from a wheel underneath the centrifuge to a pulley system which is rotated by an electric motor. The tubes are filled in the same way as the hand centrifuge and the rotation accomplished by the motor. Accurate balance in the loading is, of course, essential. The speed varies from 3,000 to 5,000 r.p.m. The constituents are then separated according to their densities and decanted off.

In a laboratory experiment amylose solution was separated by Donovan and Reilly from amylopectins (starch constituents) after heating the frozen starch paste to 60° in water, by using the above electric centrifuge.

Fig. 8 (IV *) shows a small high-speed centrifuge devised by Mack.[1] It is driven by a compressed air turbine 7·5 cm. in diameter, mounted on a vertical steel spindle. The centrifuge is mounted inside a large barrel with heavy concrete walls. The turbine is impelled by four nozzles, placed 90° apart and connected through control valves with a high-pressure air line. When the two buckets are loaded with water a speed of 9,000 r.p.m. may be attained. With lighter buckets a higher speed is possible. In the centrifuge a bowl is rotated at a high speed by a horizontal pulley fixed to the
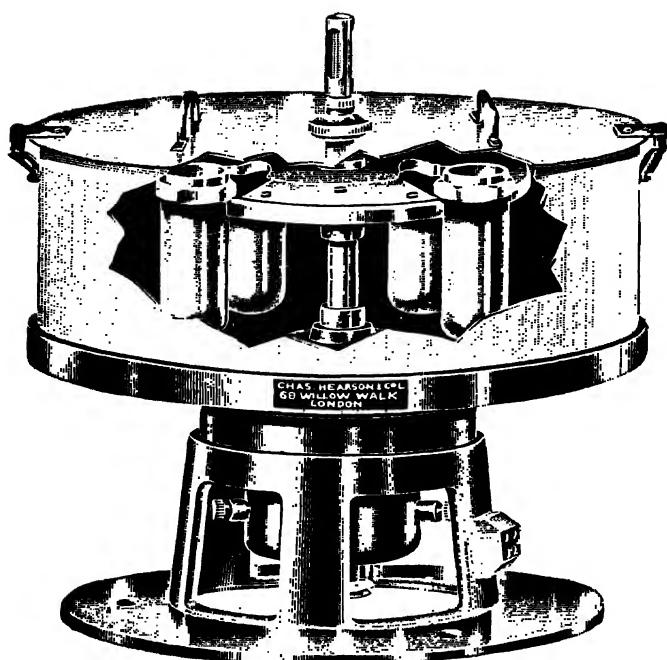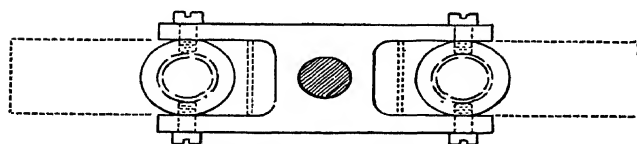
[1] *J. Amer. Chem. Soc.*, 1927, *49*, 135.
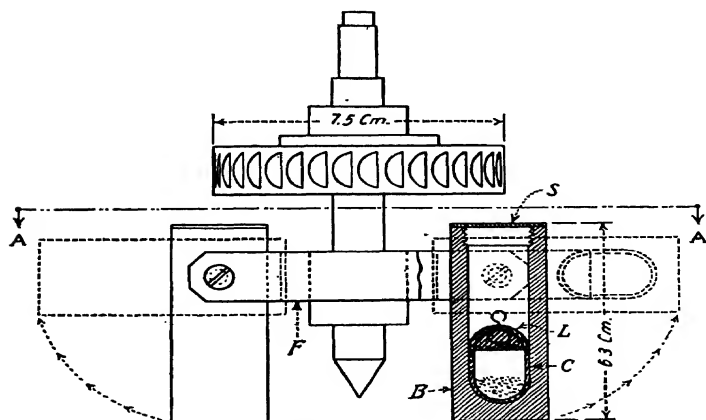
FIG. 7 (IV *)

Section at Line A-A

FIG. 8 (IV *)

bottom of the bowl. The liquid is introduced through a nozzle on the cover and a tube leads from the centre of the bottom of the bowl through the cover. During the rotation separated liquid is forced out through this tube.

LABORATORY SUPER-CENTRIFUGE

The Sharples Laboratory Super-Centrifuge is an instrument for the application of very high centrifugal force to liquids. This machine does not resemble the tube or bottle centrifuge as it is continuous in operation. The liquid is passed continuously through the rotating member or bowl, which revolves at 40,000 r.p.m. and generates a centrifugal force 1,000 times the force of gravity so that the liquid is continuously discharged.

In this way the volume of liquid which can be treated per hour is limited only by the rate at which a proper centrifugal treatment may be effected (Fig. 9 (IV *)).

The functions of the machine are :

(1) Centrifugal clarification—the removal of solid suspended matters from liquids.

(2) Centrifugal separation—the separation of materials and immiscible liquids.

This type of machine can be driven either by steam, compressed air, hand or electric motor, and can be furnished with one of three types of bowl, as follows :

Clarifier Bowl for clarification. This has one set of outlets at the top and is used for the removal of suspended solids from the liquid. The solids extracted from the liquid are retained in the bowl, the liquid flowing out of the top outlets. The solids can be removed from the bowl at the end of the run.

Separator Bowl. This bowl has two outlets in the head, or top, and is used for the separation of emulsions and immiscible liquids into their component parts, the two separated liquids discharging from their respective orifices in the top of the bowl and the solids remaining in the bowl for removal after the run.

Batch Bowl. This bowl has no discharge outlets and is arranged for handling small amounts of liquid in a batch or discontinuous manner. The small amount of liquid fed into same is submitted to centrifugal force, and on stopping the machine, drains out, leaving the solids adhering to the inside wall of the bowl. Some of the problems to which the Super-Centrifuge is particularly well adapted are as follows :

(a) Aniline—Separation of water. (b) Benzene—Separation of water. (c) Condensate—Recovery of oil. (d) Cresylic Acid—Separation of water. (e) Fusel Oil—Separation of water. (f) Nitro-benzene—Separation of water.
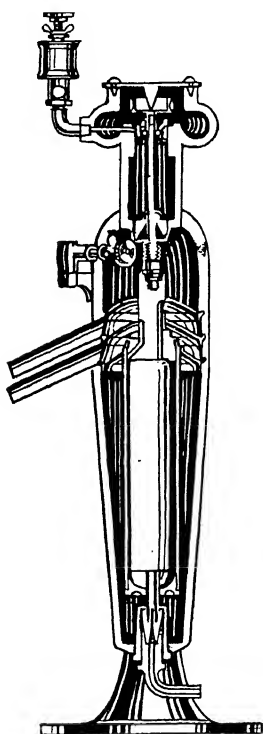

FIG. 9 (IV *)

(g) Oil Emulsions—Separation. (h) Phenol—Separation of water and salts. (i) Resin—Separation of impurities. (j) Serum—Separation of corpuscles.

ULTRA-CENTRIFUGES

Particularly in physical chemistry and biology, it is frequently desired to isolate traces of active materials occurring in a large bulk of substance, with properties, chemical and physical, so nearly approaching those of the active product, that the ordinary methods of isolation fail; or it is desired to segregate molecules in every respect identical except in a small difference in mass. It is obvious therefore that with a means of increasing artificially the force of gravity on each particle the resolution of a complex aggregation of particles only slightly differing in mass might be accomplished. This has been realized in a large measure by the development of mechanical methods for producing high rotational speeds and centripetal accelerations in excess of 8 million times gravity have already been obtained by the new ultra-centrifuges.

These ultra-centrifuges are of three types, (a) the compressed air, (b) oil turbine, (c) magnetic ultra-centrifuges. The compressed-air type consists essentially of two co-axial cones, one fitting within the other. The outer cone, known as the stator, is supplied with a number of holes through which air is blown against flutings on the inner cone or rotor. In this way spin is given to the rotor so that it lifts slightly from the outer cone. It is restrained from plying vertically both by its own weight and by the Bernouilli forces developed by the stream of escaping air at high velocity, which cause it to be pressed

FIG. 10 (IV *)

down by the pressure of the atmosphere. The effect is thus to reduce friction to an absolute minimum so that the rotor rides upon a thin cushion of air. Fig. 10 (IV *) illustrates an ultra-centrifuge of this type adapted for the separation of isotopes by evaporative centrifuging; Fig. 11 (IV *)[1] illustrates a type for use in biochemical researches. C is the container for liquid or gas and rotates in a vacuum chamber. It is provided with a flexible shaft, A, which may be hollow where withdrawal or addition of liquid or gas is desired either under vacuum or when the centrifuge is spinning. G_1 and G_2 are two vacuum-tight oil glands which increase the flexibility of the shaft A; G_1 seals off the vacuum chamber; G_2 enables liquid or gas to be removed while the centrifuge is spinning. Vacuum pump oil is forced into G_1 and G_2, and at G_1 the oil
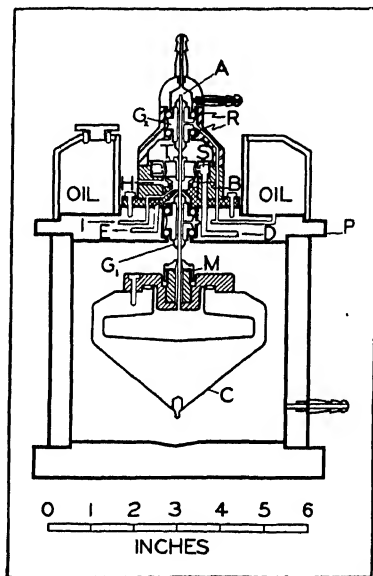
[1] Beams, *J. Appl. Physics*, 1937, 8, 795.

acts as a cooler, removing heat developed by friction to the plate P. T is the turbine or rotor with a number of flutings on its periphery. S is the stator and has a number of channels bored to direct the air blast against the flutings of the rotor; these channels have their axes in a horizontal plane and are directed so as to approximate to but not coincide with a radius of the rotor. The number of flutings in the rotor does not coincide with the number of channels in the stator and if the one is even the other is odd or vice versa. B is a cone-shaped collar and with the under surface of the rotor forms the chamber for the air cushion which supports the rotor when air is forced through I. The driving air is admitted through the channel D to the stator, S, and causes the centrifuge to spin. The limit to the speed of rotation possible is set by the mechanical strength of the rotor and rotating vessel, which on account of the enormous gravitational fields generated are shattered with explosive force if their bursting strength is exceeded. The speed of rotation is usually measured by a stroboscopic method. Centrifuges of this type accelerate remarkably smoothly, spin extremely steadily and exhibit very little wobble or vibration. Where observation of the contents of the rotating vessel is desired, an apparatus of similar design with the rotating vessel, in this case, above the rotor is used and is known as the Inverted Ultra-Centrifuge. In place of compressed air the apparatus may be driven by superheated steam.
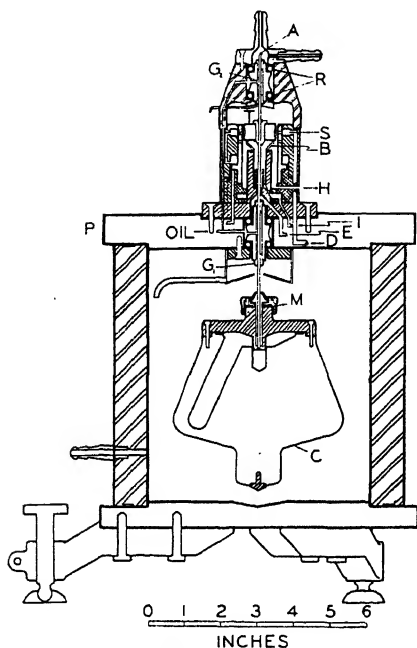
FIG. 11 (IV *)

(b) The oil turbine centrifuge developed by Professor Svedberg is spun by twin turbines on each end of a large rigid shaft. The centrifuge is supported in bearings and is shaped for maximum strength and must be dynamically balanced. It spins in a hydrogen atmosphere of low pressure and has been used to determine the molecular weight of proteins, &c.

(c) In the magnetic type of ultra centrifuge [1] a rod of iron is supported vertically by the magnetic force of one or more solenoids carrying electric current which is regulated by photoelectric cells so as to maintain the rod at a predetermined height. The rotor is attached to the rod and is spun by the action of the field of a small magnet mounted horizontally on an air-driven turbine which spins below the rotor.

Systems which are inherently convectionless, such as jellies, curds, and liquid crystals may be studied by the ultra-centrifuge. McBain and

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[1] Holmes, *Phys. Rev.*, 1937, *51*, 689; *Rev. Sci. Inst.*, 1937, *8*, 444.

O'Sullivan[1] have developed the air-driven spinning top of Henriot and Huguenard[2] as a quantitative and transparent convectionless ultra-centrifuge for such studies. It is possible to photograph the cell by transmitted light of any monochromatic wavelength visible or ultra-violet.

The influence of colloids and surfaces (electrical properties) in relation to flotation have been investigated by Wark.[3] In his book, there are discussions on variables of flotation, physical principles involved, experimental methods in flotation practice and classification of flotation reagents.

[1] *J. Amer. Chem. Soc.*, 1935, *57*, 2631.
[2] *Compt. rend.*, 1925, *180*, 1389, and *J. Phys. Radium*, 1927, *8*, 433.
[3] Principles of Flotation, *Austr. Inst. of Mining and Metallurgy*, 1938.

SECTION 3: LABORATORY FILTRATION.

The uses of the ordinary filter funnel with filter paper, or of special funnels such as the Hirsch or Büchner with filter paper or porcelain plates, in conjunction with the filter pump, are so well known and simple in their operation as not to need detailed description. Small slabs of rubber with perforations may also be used to hold the funnel in place of using cork or rubber stoppers. They are held in position by suction. The use of sintered Jena or quartz discs and 'Alundum' plates in place of cellulose filters is also a distinct advantage in the filtering of active liquids. The preparation of similar discs of pyrex glass has also been described.

The Stream-line filter [1] has been mainly applied to Motor Diesel Engine Transformer and Vegetable Oils. It also effectively discharges very thin, slimy deposits. No filter aids are necessary with this filter, but it also is not suitable for handling any great bulk of solids, nor for cases where a dry discharge is required.

For the filtering of hot solutions a short funnel is usually employed with hot-water or hot-air jacket, or the funnel may be surrounded with a core of lead tubing wound round, and through which hot water circulates. Electrically heated filter funnels made in porcelain are also available.[2] Small filter presses on the lines of the large industrial presses have certain uses in the physico-chemical laboratory, and they are considered in the next chapter. In filter paper the openings or pores in the paper are usually of the order of 1.5μ–5μ. With porcelain filters the pores may be as small as 0.2μ. These openings are comparatively large when compared with the size of colloidal particles. For the latter special types of filter (ultrafiltration) are required.

Solid carbon dioxide offers a simple method for the filtration of a substance which is liquid at low temperatures from one which is not. The cold mixture to be filtered is pressed through a layer of solid carbon dioxide on a porous plate. The precipitate has the advantage in many cases that (a) it does not adhere to the porous plate and may be easily removed, and that (b) the filtering medium disappears spontaneously from the precipitate by evaporation and that (c) easily oxidized substances in the filtrate and precipitate are protected from the air by carbon dioxide gas.[3]

One special type, the stream-line filter, requires some mention. With this apparatus very fine precipitates (such as barium sulphate precipitated from cold neutral solution and then diluted) are completely retained in the stream-line filter. Various aniline dyes and many colloidal suspensions

[1] Made by the Stream-line Filter Co., London.
[2] Berlin Porcelain Co.
[3] *Ind. and Eng. Chem. News*, ed. 1937, *15*, 21, 474; *J. Amer. Chem. Soc.*, 1935, *57*, 1990.

are unable to enter the interstices between the sheets in the filtering pack, and may in consequence be separated from the liquor in which they are suspended. The working of this filter, which has been evolved by Professor H. S. Hele-Shaw, depends on the fact that if a number of sheets of fibrous material of uniform size are pressed together complete contact is not brought about on account of the roughness of the fibrous surface and liquids under pressure may be made to pass between the sheets (usually of water-proofed paper, and rectangular in shape for economy in material), while particles of suspended solids are retained at the edge of the paper where the liquid enters. Increased filtering edges are secured by perforation of the sheets, usually in the form of large and small holes (closed at one end) arranged so that the holes form tubes through the pack. The flow of liquid, under pressure, through the channels formed between the sheets takes place without turbulence and 'stream-line' motion is secured. This edge filtration, as opposed to filtration through the body of porous textile or granular material, depends upon the power of regulating the attenuation of the films in which the fluid passes with the stream-line motion.
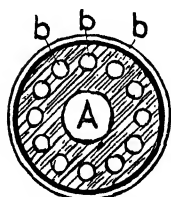
FIG. 12 (IV *)

FIG. 13 (IV *)

Diagram   Section.
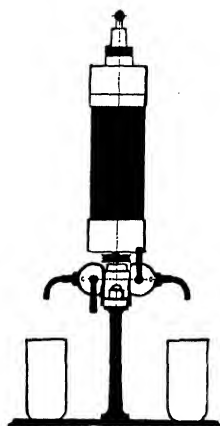
FIG. 14 (IV *)

Comparatively high working pressure may be readily employed without great mechanical difficulties or risk of bursting the tubes.

In Fig. 12 (IV *) are shown small circular discs where A represents the inlet for the liquid to be filtered and b b b the outlets. A diagrammatical section is also shown in Fig. 13 (IV *). In Fig. 14 (IV *) a laboratory form of this 'Hele-Shaw' filter is shown. The pump for securing the pressure is inserted in the centre tube of the sheets and the operating handle is at the top of the apparatus. An external pump may also be used, and it is especially useful when large quantities of solids require removal. The arrangement of a three-way tap enables the direction of flow to be reversed. In the latest form of instrument the pack pressures and pressure of filtration may be adjusted and recorded with accuracy and a complete control of operations secured so that experiments may be repeated accurately if neces-sary. The pressure on the pack is exerted by the compression of a spring which can be adjusted accurately by means of a screw of fine pitch and large diameter. The outer surface of the pack where the liquid leaves after filtration may be exposed and the flow watched. After filtration the solid can be removed without disturbing the pack.

Metafilters. Another system of filtration which can be applied to both

laboratory and technical problems is that known as the metafiltration method. This filter is suitable where relatively small amounts of very fine solids require removal. It can effectively discharge very thin, slimy deposits and the leaves are specially adapted to maintain a pre-coat of , filtrate in position and discharge it when required.[1]

The basis of all metafilters lies in filtering members which are built up
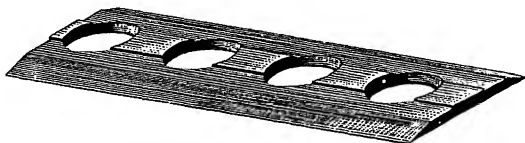
FIG. 15 (IV *)

from a number of metafilter strips or rings. These filtering members may be of almost any size from many square feet down to a few inches, and they are varied in their shape, disposition, and method of attachment to suit the requirements of the most varied types of duties.
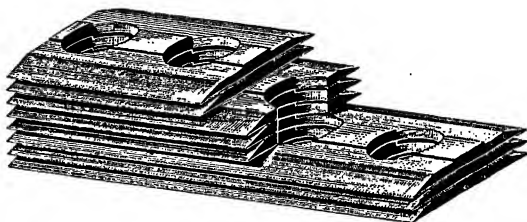
FIG. 16 (IV *)

Filtering elements may be built in practically any material such as bronze, steel, ebonite, &c., in strips such as that shown in Fig. 15 (IV *).

The filters may be designed to work under pressure in closed containers or under vacuum in open containers, and generally speaking filters can be
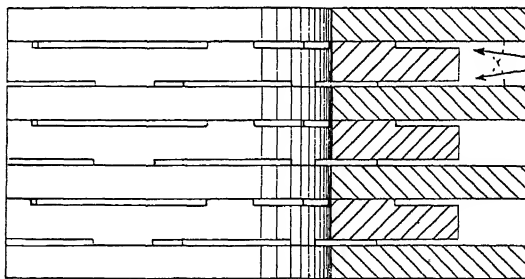
FIG. 17 (IV *)

built with the metafilter unit as the essential part of the filter, the other details following the general lines of almost any other type of filter employing cloth or other medium.

When the strips are piled upon one another and tightly held in contact (Figs. 16 (IV *) and 17 (IV *)), the perforations come into register and

[1] Messrs. Metafilters, Ltd., Hounslow, Middlesex, have supplied data for above and provided the electros.

form internal drainage channels through the whole assembly. It will be seen that the strips are separated by the precise height of the ribs, which may be 0·0005 to 0·0030 inch. This dimension determines the fineness of the filter. The bevelled edges of the strips form **V**-shaped grooves all over the surface of the filter, and these grooves have
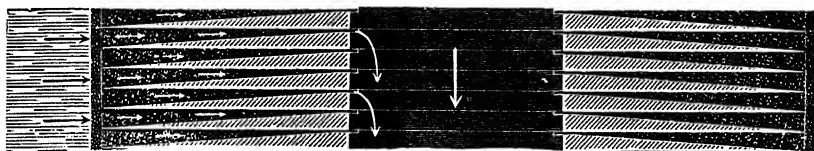
FIG. 18 (IV *)

special advantages in preventing choking and assisting in easy cleaning. The liquid which is being filtered is caused to pass from the wide end to the point of the **V**-shaped grooves into the internal drainage channels, solid matter being retained in the grooves (Fig. 18 (IV *)). A filter bed is usually deposited in the grooves over the whole surface before commencing operation. The liquid leaves the internal drainage tubes by a channel which is provided in the lower member of the frame communicating with a spigot. The strips are held in position by compression between a top bar and the grooved lower bar, being retained at the sides by the slotted side bars which carry tightening-down nuts at the upper end.

In cases where a column form of filter is to be preferred to a flat surface, metafilter rings may

FIG. 19 (IV *)

be employed. These may be made with bevelled periphery and raised projections at the flat centre.

In other cases the bevelled channels may be provided in a simpler way by interspersing plain rings of larger or smaller diameter between rings carrying projections on both the upper and lower surfaces.

A filter of the strip type for laboratory use is shown in Fig. 19 (IV *.) It is contained inside a rectangular tank to which the liquid to be filtered
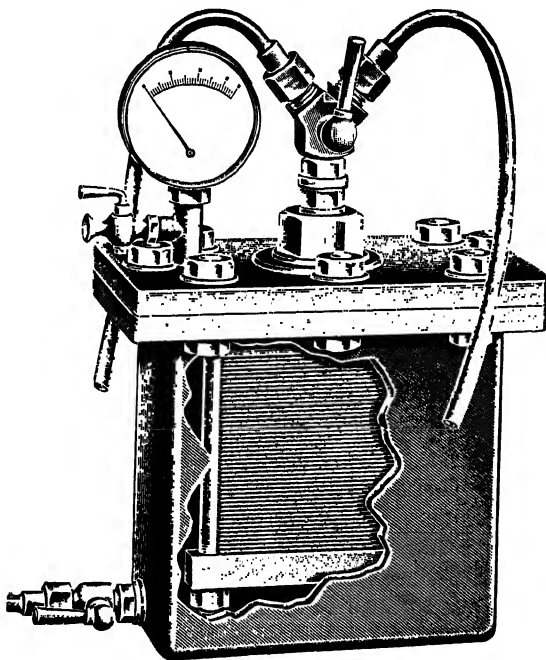
is supplied under pressure. The filtered liquid leaves the filter by the spigot exit at the top, the filtrate being delivered by one or other of the two pipes through the two-way tap. The object of the two-way tap is to enable the first runnings to be easily separated from the main bulk. The filter is provided with a pressure gauge, petcock, and inlet control cocks.

Where filtration under vacuum is desired, the filtering pack can be withdrawn from the container and utilized by connecting to a vacuum suction flask. It is only necessary to immerse the filter in the liquid to be filtered and to draw this through into the vacuum flask. If it is desired to separate the first runnings from the main bulk, two flasks may be employed, one connected to each of the delivery pipes.

A filter constructed as above from rings or strips is capable of fineness of filtration down to particles of about 0·0005 inch or somewhat smaller, but this is not exacting enough for removal of bacteria and the clarification of most hazes. In these cases it is found better to employ in conjunction with the metafilter, a filterbed deposited in the V-shaped grooves and covering the metafilter up to beyond the edges of the strips or rings. A very large variety of materials may be used for bed formation, of which calcium and magnesium carbonates, kieselguhr, powdered charcoal, and animal charcoal are some of the most useful. A filter frame in part section assembled with drainage channels is shown in Fig. 20 (IV *).
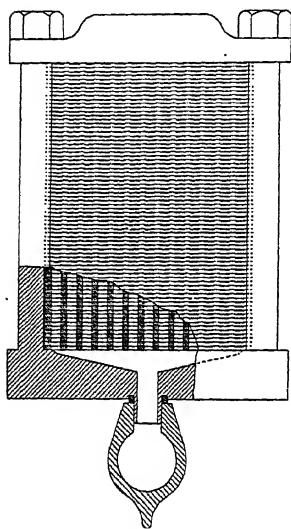
The process of forming the bed is simple. The filterbed material, e.g. specially selected powdered charcoal, kieselguhr, decolorizing carbon, magnesium carbonate, is mixed in the right amount with water or other liquid which is to be filtered and poured into the filter container. The liquid is then passed through in such a way as to stir up and maintain the suspension of the filterbed material, which is quickly carried forward and remains lodged in the V-shaped channels which cover the surface of the metafilter. In some cases it is possible to go straight on with the filtration when this has been done. In other cases it is better to drain the water used in bed formation from the body of the filter and follow on with the beer or other liquid to be clarified.

FIG. 20 (IV *)

Metasil is a porous filterbed containing a specially selected and purified variety of kieselguhr, and is supplied packed in any desired form, but usually in cases of 12 packets each containing 3 lb. of metasil. This material is made specially by Metafilter, Ltd.

Press filtration is considered in the next section and the various types are briefly classified.

Ultra-filtration (see also chapter on Colloids). Collodion in ether alcohol solution is used for filters for colloidal solutions. The solution is placed on a filter cloth or on unglazed porcelain for support. Special

devices may be used to give support where the filtration is carried out under pressure. The membrane consists of cellulose nitrate dissolved in alcohol-ether-acetic acid mixture.

These gelatinous esters of cellulose filters are known as *Sieve* filters. Another type known as *Adsorption* filters consist of a material manufactured mechanically from asbestos, kieselguhr, porous earth, &c. The ultra-filters of Zsigmondy [1] possess a glazed flat surface so that all precipitates can be separated quantitatively. They are comparatively compact, combined with a certain elasticity so that the same filter may be used repeatedly. Although the pores are very fine, the filter has a rapid rate of filtration. In the manufacture of these filters it is possible to control the size of the pores and a large range of filters of different porosities is available from a medium pore of about 1 μ down to pores which will retain quantitatively certain aniline dyes and albuminous molecules. [2]
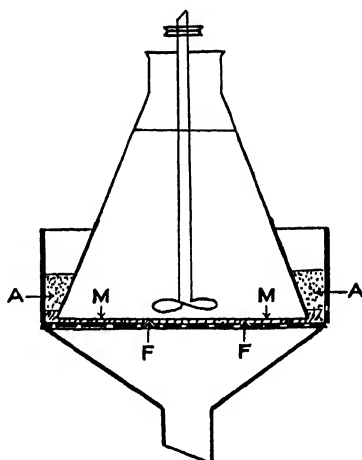
FIG. 21 (IV *)

An ultra-filter of the type designed by Bechhold is made by Carl Schleicher and Schull and impregnated *in vacuo* with acetic acid-collodion with varying contents of cellulose nitrate in the collodion. The filters are kept before use in a metal case closed with a rubber ring, and each paper is placed between parchment paper and is surrounded with a very dilute aqueous solution of chloroform to keep the paper moist and to prevent the growth of bacteria or moulds. The permeability of these papers to various colloids depends on the cellulose nitrate content, e.g. a 4·5 per cent ultra filter will prevent the passage of haemoglobin from a 1 per cent solution.

These discs are placed in a Büchner funnel as in Fig. 21 (IV *) at M and filter paper at F, and melted paraffin inserted around funnel at A to make an air-tight joint. It is necessary with certain colloidal solutions to keep them agitated during the ultra-filtration; otherwise precipitation may occur.

[1] Can be supplied by Maempel, Finsbury Pavement House, London, E.C.2.
[2] See also Jander and Zakowski, *Membran-cells und Ultrafeinfilter*, Leipzig, 1929, and Zsigmondy, *Kolloid Chemie*, 1925, 5, Part 1, p. 26.

SECTION 4: PRESS FILTRATION [1]

This section gives a short description of filter presses which are mainly intended for semi-technical chemical engineering operations. They serve, however, for certain purposes in physico-chemical work.

A filter press plant consists of one or more filter presses with a pump or its equivalent, together with suitable connecting piping and storage vessels.

Filters may be divided into various types, generally as follows:

(a) Chamber and Frame Presses.
(b) Enclosed Filters Leaf Type.
(c) Enclosed Filters with special elements.
(d) Enclosed Filters Deep Bed Type.
(e) Pulp Filters.
(f) Sterilizing Filters.
(g) Vacuum Filters:
    1. Backs or Nautches.
    2. Tank Type with Leaves.
    3. Rotary Continuous.

Pressure Filters. Probably the most common type is the Chamber (or Recessed) Press, and its variant the 'Frame' Press. These presses are adaptable to almost every problem, including filtering solids from liquids and high-speed clarification. The cake may be washed or air dried (Fig. 22 (IV *)). The presses may be heated or cooled and many other modifications are possible. In general this type gives the driest cake. The cloths are readily changeable. The type is suited to both low and very high pressures. The capital cost of the filter area is low compared with other types. The plant is simple and foolproof.

This type of press is not suitable for very volatile products on account of the large number of joints through which vapour can escape. The cloths are subject to a good deal of pressure on the joint surface which makes for wear and tear. The most important defect is that the cost of discharging becomes important for large-scale work, particularly in instances where the filtering cycle is short. Washing is limited as compared with certain other types, because the thickness of the cake which has to be traversed by the liquid during washing is double the filtering thickness, and if the cake cracks or channels there is no means of making this good and then some of the wash liquid short circuits.

The *Recessed or Chamber Presses* are built up of a number of plates which are recessed internally and have raised rims (Fig. 23 (IV *)). The faces are covered with drainage grooves which connect through ports to outlet nozzles or taps. The plates are covered with cloths which are sewn together to make a joint at the feed opening. If the cloths are not to be

[1] The data for this section and electros were kindly supplied by Mr. E. A. Alliot.
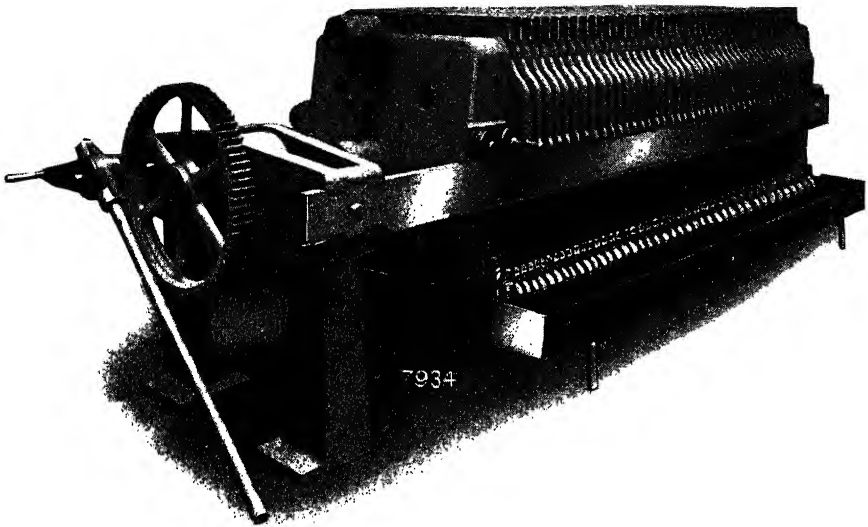
FIG. 22 IV *)

frequently changed the joint may be made by a cloth clip. This saves expense in preparing the cloths, but takes more time than the double cloth arrangement.

Chamber presses are not suitable for making thick cakes, 1·25 inches to 1·5 inches thickness being usually the limit ; very deep chambers strain the cloths.
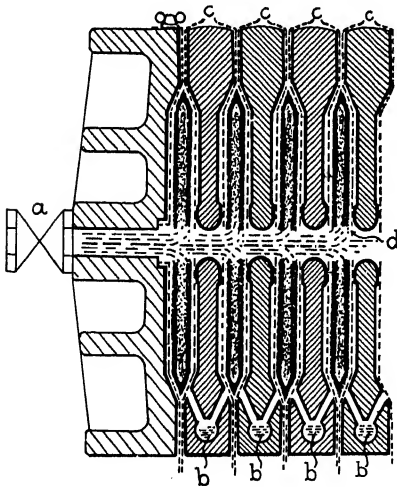
Frame Presses are more costly, but the cloth lies flat on the plate and is not subjected to strain. Thick cakes can be made in this type of press, but there are difficulties with thin ones. As a rule it is convenient for frames to be 1 inch thick or over. Frame presses call for more labour than chamber type, because of the additional number of elements, but where the cloths must be frequently changed frame presses with the passages in external lugs (Fig. 24 (IV *)) make for economy in labour since plain unperforated cloths can be used with cloth sleeves or rubber joint

FIG. 23 (IV *)

rings on the lugs, thus much simplifying the preparing of the cloths, the act of re-clothing, and the ease with which the cloths are put on in the correct position. Washing is better as a rule in frame presses than in chamber because of the even thickness of the cake. Provision should be made for eliminating air. The wash water is usually admitted at the bottom corner

of the press and taken away from a top corner. In this way the hydro-static head is balanced. It is a good plan to have a ledge or labyrinth
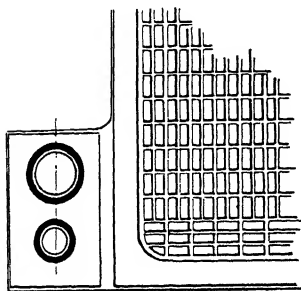
FIG. 24 (IV *)
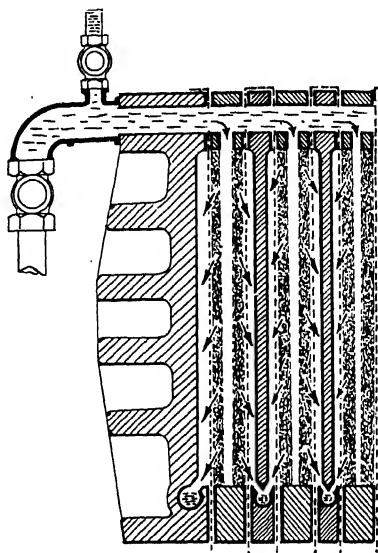
FIG. 25 (IV *)

round the inside of the frames on the wash-water outlet side to act as labyrinth joint against leakage should the cake shrink a little (Fig. 25 (IV *)).

It is an advantage in many presses to have a plate to act as a false head to isolate any required number of chambers so that firm complete cakes can be made in only a part of the total number of the chambers if a smaller batch of material has to be treated.
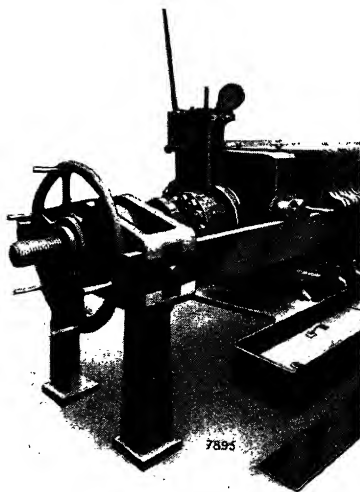
In both frame and chamber presses the plates can be made with internal passages for heating or cooling.

A variety of closing devices are used, plain lever and centre screw sufficing for small presses, and ratchet wheel with spur wheel and pinion for larger ones. Hand-power hydraulic closing with hydraulic pump on the loose head is a very satisfactory method where high closing pressures must be applied (Fig. 26 (IV *)). An economical number of chambers in a filter press depends on the length of the filtering period. If filtering periods are short the press must have

FIG. 26 (IV *)

comparatively few chambers, otherwise the time of emptying will be out of balance with the rest of the cycle. Where filtering and washing take a long time the press may have a much greater number of chambers.

Enclosed Pressure Filters of the Leaf Type, such as the Kelly, Sweetland, Easifilt, and other types, are specially adapted for high-speed clarification, and also for large-scale removal of solids from liquid where the produce filters freely at moderate pressures. The great advantage of these presses is the speed with which they can be discharged. The rate of filtration is usually high because the cakes are not consolidated under pressure and are not permitted to meet. Washing is speedy and excellent for the same reason, and also because channeling and cracks due to cake shrinkage can easily be made good. The cloth wear is light, since the cloths do not need to take jointing pressure. Moreover, because the press has a single joint it is very suited for volatile products; the construction is also suitable for liquids which must be kept hot or away from air, or
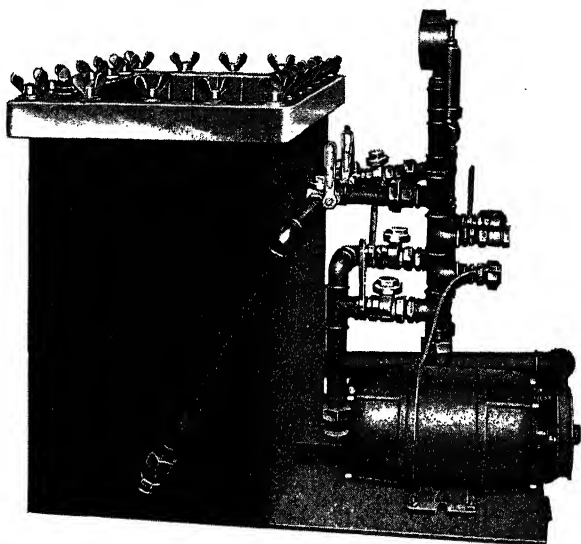
FIG. 27 (IV *)

those which contain gas under pressure. The capital cost is high for small-scale operations, but as a rule low for large-scale operations on suitable products.

As a rule, cake from this class of filter is less dry than that from plate and frame filters. Moreover, filter liquor remains in the press at the end of filtration and this must be removed by draining or by air blowing. The cake may readily drop from the leaves unless care is taken to always maintain positive pressure in the press while switching over from filtration to either washing or drying. It is usually necessary to take special precautions to close up cracks in the cakes if washing is desired. This type of press is not well suited to cakes which cling to the leaves and do not drop away readily when, for instance, air is blown back through the filter leaves. The type is also not suited where the cloths clog rapidly. It is necessary

to be careful when operating the press not to allow cakes on the leaves to join, if they do discharge will be cumbersome and leaves may be bent.

Another type of leaf filter is the ' Clearflo Filter' (Fig. 27 (IV *)).

The special features of this filter are that the liquid to be filtered is passed through the filter by vacuum created by the circulating pump. Consequently the pump only handles clean liquid, and is not subject to possible damage by handling dirty liquid which may contain abrasive matter.

The filter leaves are covered with cloth bags which are provided with a mechanical means of scraping off the deposit without opening up the filter. Consequently this filter may run for very long periods without having to be opened up for cleaning purposes, as an ample sump is provided at the bottom for containing the dirt scraped from the leaves, which dirt can be removed from a door at the bottom of the filter.

The filter is particularly adaptable for filtering large quantities of solvent used in dry-cleaning plants.

A small comparatively inexpensive filter consists of a vertical cylinder with removable cover at the top and cleaning door at the bottom. In this are placed a number of leaves of coarse wire mesh covered with cloth bags or monel metal filter cloth. The bottom of each leaf is fitted with a hollow conical projection which is at once a support and an outlet. These projections fit holes in a pipe or header placed horizontally in the filter which serve as an outlet. Liquor is admitted to the filter at the side or bottom, it fills up the space between the leaves and passes through the cloth on which the solids are left. The filtered liquor passes downwards through the coarse iron mesh and out through the outlets into the filtrate outlet header. At completion of filtration the remaining liquid is blown out by air, or drained off, after which the lid is removed and the cake scraped off into the bottom of the filter which acts as a cake sump. The filtration can now proceed again and a second set of cakes obtained after which the cake must be removed through the bottom discharge door. Such a filter will handle about 40 gallons white solvent per square foot per hour at a pressure up to about 60 lb. per square inch. In a more elaborate type the filter casing is hinged vertically and the leaves are attached to a header which can be drawn out on arms when filtration is completed and the filter is opened. A trolley can then be run underneath the leaves and the cakes scraped off. In a filter of the type having leaves arranged with both top and bottom drainage into separate sections of the header it is possible to filter dry-cleaning solvent at a rate of 80 to 100 gallons per square foot per hour. For this purpose filter aid is mixed with the solvent.

The *Kelly Filter* works on somewhat similar principle to the two filters above. The body of the filter is a horizontal cylinder and the end cover can be drawn out on rails bringing.the leaves with it.

One of the most developed large-scale pressure leaf filters is the Sweetland. This has a long cylindrical cast-iron body split horizontally, the two parts being hinged to each other. At the end of filtration the bottom part can be dropped down, after which the cake on the leaves can be scraped into trolleys or on to a conveyor placed below the filter. The filter can be

fitted with spray-pipe by means of which the cake may be washed off the leaves.

Washing in such presses can be carried out either by simply following up the feed with water, or at the end of filtration the remaining liquid may be blown out of the press. Wash water may be then introduced without mixing with the liquid to be filtered.

Unevenness of washing due to broken or cracked cakes may be avoided by mixing with the wash water a small amount of already washed cake.

The ' *Vallez* '[1] is an enclosed pressure filter in which the leaves are mounted on a hollow central shaft which revolves at about 1 to 2 r.p.m. This enables a uniform cake to be built up from slurries which are by no means free-filtering and in which there would be a strong tendency for selective settlement of solids to take place. This would cause tapering cakes of uneven resistance to be formed in filters having stationary leaves. With uneven resistance, washing is poor because certain portions have been thoroughly penetrated by the wash water and freed from solubles while the others are still only partially washed.

The ' stream line ' and the metafilter have been considered under laboratory filters.

In ' pulp ' filters, the filtering medium may be re-used almost indefinitely. The drawback is that a considerable bulk of additional machinery for forming pulp beds and re-cleaning the pulp is required. A modern form consists of a vertical vessel closed by a lid on the top and having within it a pile of superimposed pulp cakes. Liquid is admitted to the body of the vessel and passes through the cakes direct to an outlet passage. The pulp cakes are formed in a small pneumatic press and after use are washed and agitated with water in a large special tank. A somewhat similar operation may be carried out in a light type of enclosed pressure leaf filter by putting on its leaves, before they are used for filtering, a filter mass (consisting of special mixture of cotton and asbestos fibre). This is laid on the leaves in such a way that in effect it consists of a paper covering which can be peeled off intact when the leaves have to be cleaned.

Sterilizing Filter consists of special plate filter using thick prepared pads or films which are a special mixture of cellulose and asbestos fibres (Fig. 28 (IV *)). These filters are specially suited for polishing and sterilizing beverages and also for clarification where the sediment is very fine and present in minute quantities only. This type of filter is foolproof, but the films cannot be re-used. The pads are in appearance like very thick heavy blotting-paper. There are various types equal to the degree of straining or sterilization required. This depends a little on the type of bacillus, since a long mobile, flexible type will pass more readily than one formed like a short rigid rod. Filters of this kind can be used for sterilizing serums, antitoxins, liver and other extracts which cannot be sterilized by heat.

Before treatment in this filter liquid must have been pre-filtered to remove all except the very finest residue solid matter. Such filters are foolproof because it is impossible for the liquid to get to the discharge side of the filter without passing through the pads, which are not easily ruptured providing pressure is not allowed to become excessive.

[1] Made by Messrs. Watson, Laidlaw & Co., Ltd., Glasgow.

Vacuum Filters. Tank type of filters usually known as a ' Back ' or ' Nautches ' are convenient for small-scale filtration when the solids build a thick cake easily. They are not suited to large-scale operations or difficult filtration. The construction is simple. All that is required is a tank with suitable filter surface laid on the bottom and jointed well round the sides and a suction connexion either to a wet vacuum pump or to a dry pump with torricellian or other connexion. Then we have the type in which a number of leaves hang from a header and are suspended in a tank containing the liquid to be filtered. Suction is applied to the interior of
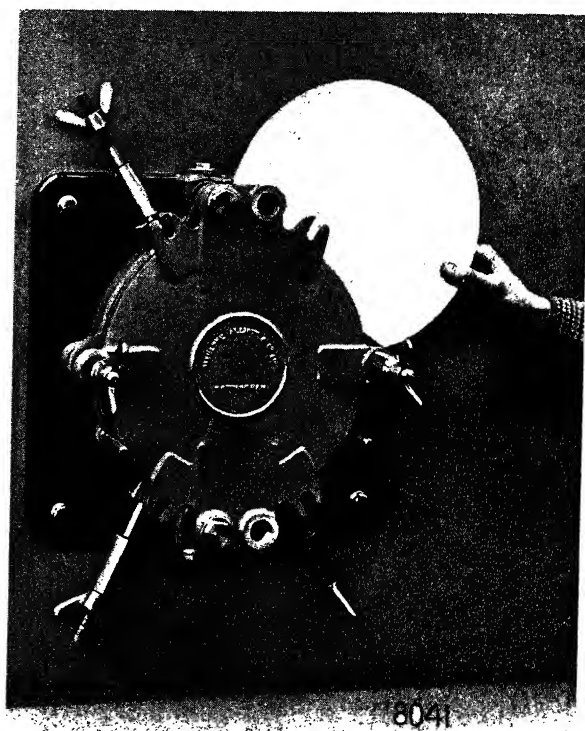
FIG. 28 (IV *)

the leaves; when they are covered with cake they are lifted out of the tank and transferred to a wash-tank.

The *Moore Filter* and *Butters Filters* are variants of this type. Rotary continuous vacuum filters have very high capacities when operating on suitable problems. Practically no labour is required. This type of filter is used for handling large-scale filtration where the solids are free-filtering. Good displacement wash is obtainable with this class of filter and the capital cost is relatively low when employed on large-scale work.

Such presses need to be fed with well-concentrated slurry. The time available for the divisions of the solubles from the interstices of the solid particles during washing is very short. The capital cost is very high

if the operations are conducted on a small scale. The surface of the modern rotary filters is divided into sections which are placed under suction while they revolve through a tank containing the material to be filtered. As they emerge from the tank they are usually subjected to washing by means of spray pipes. As they rise higher and come near the discharge point air is drawn through the cakes in order to dry them as far as possible. Finally each section comes opposite a knife or ' doctor ', which scrapes the cake off. During this process it is usual to subject the cake to a blast of air in order to free it from the cloth. The heart of this arrangement is the rotary valve, by means of which the outlets from the various sections are connected first to vacuum through a port connected to filtrate receiving tank, then to vacuum through another port connected to a washings receiving tank.

There is also a port for compressed air. The slurry tank is usually provided with an agitator to prevent mud from settling.

In certain recent developments a number of endless strings are passed over the drum about 0·75 inch apart. The cake is built over these and as they are passed over a discharge roller at the side of the filter they strip the cake off the filter and the cakes drop away from the strings as they pass over a small individual roll on their way back to join the main filtering roll as it passes through the trough again. This strips the cloth without forcing the cake into its ports, as is liable to occur when a scraper is used. The cloth therefore retains its filtering quality longer and filtration is more rapid with some materials. In a variant of this device a flexible wire made of very open weave is used which can either pass over the rollers or be taken in festoons through a drying chamber.

In order to prevent cracking of cake during drying a wide canvas band is sometimes stretched over in such a way that it presses on the upper surface of the filter cake, helping to compress and close down any cracks.

For further information on various types of rotary continuous filters and their working, see Badger and McCabe,[1] *Elements of Chemical Engineering* (McGraw-Hill, 1931), section on Rotary Continuous Filters ; or the latest edition of Perry's *Chemical Engineering Handbook*, section on Continuous Vacuum Filters and Motors.

Fifteen separation processes have been outlined in the last three chapters, but this does not exhaust all the possible practical methods available to the Physical Chemist. References will be, however, limited here to only one other process, namely, separation or elimination by diffusion. This method of separation is of special importance in biological research where analysis of such products as ammonia require estimation even when only very small amounts of material are available. The ammonia is separated by diffusion from one chamber in which it exerts a certain tension into an absorbing fluid in another chamber in which the tension is reduced to zero. The diffusion conditions for many cases have been worked out by Conway [2] and special design of standard diffusion apparatus or unit of his design are

[1] *Elements of Chemical Engineering*, McGraw-Hill, 1931.
[2] *Micro-diffusion Analysis and Volumetric Error*, London, Lockwood, 1939.

now available.[1] According to Conway the micro-diffusion process has been found of value for the following determinations :

(a) Ammonia, including special application to normal blood ammonia determinations
(b) Total nitrogen
(c) Adenylpyrophosphoric acid
(d) Adenylic acid (muscle)
(e) Adenosine
(f) Aliphatic amines
(g) Chlorine, Bromine and Iodine
(h) Alcohol and Acetone
(i) Carbon dioxide—with application to determination of (1) blood bicarbonate or 'alkali reserve', (2) oxidation rates of organic substances in vitro.

A new section on general diffusion methods and the apparatus employed will be given in the Supplementary volume. For an excellent description with practical working details of the micro-diffusion method the text of Conway can be strongly recommended. This book gives an account of apparatus and principles used, including a description of the Kirk 'drop-scale' technique.[2] An excellent bibliography is also included.

[1] *Microchemie*, 1934, *16*, 26.
[2] Obtainable from A. Gallenkamp & Co., Finsbury Square, London. For details of unit, see *Biochem. J.*, 1936, *27*, 420.

CHAPTER V *

COLLOIDS

SECTION 1: PRACTICAL METHODS IN COLLOID CHEMISTRY

THE study of colloid chemistry has developed to such an extent within the last twenty years that the subject is now comparable in importance with any other division of chemistry. For this reason it might be accounted outside the scope of this volume, but it is felt that any work on physical chemistry must necessarily be incomplete if it holds no reference to this important branch.

General Conditions. Owing to the sensitiveness of colloids to the presence of small quantities of electrolytes, practical work must be carried out with extreme care to the exclusion of any such impurities. Distilled water must be used in all cases, the specially pure *conductivity water* in some cases being necessary. The water should be freshly distilled if possible. For storing water or colloid solutions resistance-glass vessels must be used; solution from the walls of inferior glass supplies sufficient electrolyte to precipitate a colloid. The utmost cleanliness must be observed, all vessels being cleaned and steamed out before use.

Methods of Preparation. The preparation of inorganic colloidal solutions can roughly be divided into two groups:

(1) Condensation methods.

(2) Dispersion methods.

Condensation Methods. In the methods under (1) the colloid is produced by the aggregation of molecules originally in true solution; this is accomplished by chemical methods, so the group can further be subdivided into:

(*a*) Methods of reduction. (*b*) Methods of oxidation. (*c*) Methods of hydrolysis.

There are very few condensation methods which do not come under one or other of these generalizations.

Dispersion Methods. In the methods grouped under (2), substance in bulk or coarse suspension is broken up or dispersed in the continuous medium to colloidal dimensions. This can be accomplished by:

(*a*) Purely mechanical methods.

(*b*) Chemical and mechanical methods.

(*c*) Electrical methods.

A few typical preparations of colloidal solutions illustrating these methods will now be described.

Condensation Methods: (*a*) Reduction: Preparation of Colloidal Silver by the Method of Carey Lea. · 200 ml. of a 10 per cent solution

of silver nitrate are placed in a precipitating vessel. In another vessel
are mixed 200 ml. of a 30 per cent solution of pure ferrous sulphate and
280 ml. of a 40 per cent solution of sodium citrate. Some advantage may
be gained by neutralizing the ferrous solution, which is acid, with sodium
hydroxide ; as much may be added as will not cause a permanent precipitate.
The mixed solution is then added at once to the silver solution and the
whole stirred very thoroughly for several minutes. After standing for 10
or 15 minutes the liquid is decanted, leaving a large quantity of a heavy
precipitate of a fine lilac-blue colour. It is washed by decantation or on
a filter several times with a solution of ammonium nitrate or other salt.
The precipitate instantly dissolves in pure water with an intense blood-red
colour and constitutes a colloidal solution of silver.

Zsigmondy's Gold Solution. Zsigmondy [1] has described the prepara-
tion of a gold hydrosol by a reduction method. Three solutions are used :
(1) 6 grams $AuCl_3.HCl.3H_2O$ dissolved and made up to 1 litre with con-
ductivity water ; (2) 1 litre of $0.18N. K_2CO_3$; (3) a 0.3 per cent solution
of formaldehyde. 120 ml. of conductivity water are heated and 2.5 ml.
of solution (1) added, then 3.5 ml. of solution (2). This is stirred and
heated to 100°. Then 3 to 5 ml. of the formaldehyde solution are added
with constant stirring. The amount of formaldehyde used may be varied
with resultant variations in the solution. A deep red solution is thus
obtained.

Kohlschütter Silver. Kohlschütter has reduced silver oxide in water
at 50°–60° by means of a stream of hydrogen. A 5 per cent solution of
silver nitrate is taken and silver oxide precipitated with a slight excess
of dilute sodium hydroxide solution. The precipitate is allowed to settle
and washed several times by decantation with hot water. A saturated
solution is then made in hot water, undissolved oxide being filtered off.
A stream of washed hydrogen is then passed through the solution at 50°–60°
for 40 minutes. The colloidal sol is thus obtained without the presence
of electrolytes.

Metallic Sulphide Sols. A very common type of colloid which may
be classed under those prepared by reduction is the metallic sulphide sol.
The initial work on these sols was that of Linder and Picton. The sols
may be obtained by (1) allowing the metallic solution to run into sul-
phuretted hydrogen water kept saturated by a stream of the gas. It may
then be freed from uncombined sulphuretted hydrogen by a current of
hydrogen or dialysed to free it from salts. (2) Suspending the metallic
hydrates in water and passing in sulphuretted hydrogen gas. (3) Sus-
pending the freshly precipitated sulphides in water and treating with
sulphuretted hydrogen.

By the first method the solution of any metallic sulphide may be
obtained provided no great excess of acid is present. The second method
is not always applicable, but has been used by the original workers in the
case of copper and zinc sulphide sols. The third method is applicable to
mercury or copper.

(b) **Oxidation : Sulphur Sol.** Of oxidation methods the preparation
of colloidal sulphur by oxidizing sulphuretted hydrogen may be instanced.

[1] Zsigmondy, The Chemistry of Colloids, 1917.

The oxidation may be accomplished by sulphur dioxide, in which case the sol results from both reagents. Washed hydrogen sulphide is passed into sulphur dioxide water until all odour of the latter is removed. The colloidal sulphur is precipitated by shaking with powdered sodium chloride and filtered off. The precipitate is washed thoroughly on the paper to remove the chloride, when the sulphur will tend to resume the colloidal state, running freely through the paper. The sol is thus obtained by continued washing. Colloidal sulphur is very often prepared inadvertently in inorganic analysis, when hydrogen sulphide is passed through an oxidizing solution.

(c) **Hydrolysis : Hydroxide Sols.** Colloidal ferric oxide may be obtained by hydrolysis of ferric chloride solution. The preparation is very simple. A few millilitres of a concentrated ferric chloride solution is poured into a large quantity (about 300 ml.) of boiling water. A deep red sol is immediately formed. Sols of aluminium, chromium, and stannic hydroxides may be prepared somewhat similarly from the corresponding salts. Chromium hydroxide sol is prepared by adding ammonia to a boiling, very dilute solution of chromium chloride ; chromium hydroxide is precipitated. The excess of ammonia is boiled off, the precipitate allowed to settle, filtered and washed. It is then dissolved in boiling 6N. hydrochloric acid, and the resulting solution evaporated to get the last of the precipitate into the solution. More hydroxide is then added to the chromium chloride solution, the solution filtered and dialysed to remove electrolyte. A clear green sol results.

Dispersion Methods : (a) Purely Mechanical. Many methods of forming colloids by mechanical action alone are not on record. Solid material may in some cases be reduced to colloidal size by prolonged grinding alone. The extreme degree of fineness is best secured by ' diluting ' the material with some other solid which can be finally removed by an indifferent solvent. The remaining material when shaken up with the dispersion medium disperses spontaneously if the grinding has been fine enough. Wegelin has produced colloidal sols of silicon, vanadic acid, molybdic acid, and a few other compounds by grinding in an agate mortar, sometimes with the addition of a little water. Material of colloidal dimensions is produced from bulk material on the commercial scale by means of Plauson's colloid mill.[1] The standard size of this mill is 15 litres capacity, but larger sizes have been built (Fig. 1 (V *)). It consists of several armed discs of special quality steel bolted together ; the arms pass closely, with 1 to 3 mm. clearance through gaps in stationary baffles, above and below the axis of the revolving shaft carrying the beaters. The number, width, arrangement, and clearance of the teeth may be varied. The arm wheel is rotated by a belt-drive up to 3,000 r.p.m. The material to be milled is fed in through an inlet in the form of a coarse suspension, and, becoming engaged by the revolving wheel, is subjected to the forces between the wheel arms and the baffles. With this mill ultra-microscopic particles less than 0·001 mm. diameter are obtainable.

In almost every colloidal preparation, however, the mechanical action of this mill is assisted by the addition of ' dispersators ' or ' accelerators ',

[1] A description of the colloid mill is given by Forster and Reilly, *J. Soc. Chem. Ind.*, 1922, *41*, 20.

which are claimed to be necessary for the preparation and permanency of many colloids. Their purpose is, by physical or chemical means, to allow or accelerate the disintegration of the particles and reduce the power consumed by the mill. Theoretically, their function is to absorb or to precipitate soluble electrolytes always present, although sometimes only in traces, in the material being reduced to the colloidal state. Actually, they appear to act as protective colloids. These accelerators cover a wide range of substances, as may be seen in the patent literature quoted. Another use claimed for the mill is the fractional disintegration of mixtures of substances of different hardness, enabling a ready separation of the less disintegrated ingredient by settling.

For the manufacture of colloidal solutions the mill may be run as a continuous operation. Many substances are said to be sufficiently quickly dispersed in the mill as to be capable of being run continuously through at a comparatively rapid rate. With more resistant material a continuous process is aimed at by the use of a number of mills in series.
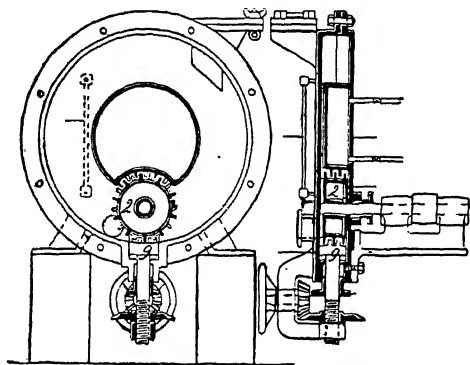
FIG. 1 (V *)

The material to be milled must first be ground in ordinary mills, ball-mills, &c., since the colloid mill cannot deal with particles too large to be caught in the small clearance between the wheel-arms and the baffle-sides. After preliminary grinding, it is then made into a suspension with water (or other liquid), in suitable proportions not exceeding the specific saturation. The accelerator, the nature and amount of which depend on the colloid to be prepared, may be added at this stage, or simultaneously run into the mill. The suspension is then run continuously into the top of the mill, the beater-wheel of which must exceed the critical number of r.p.m. for the material being milled. During the milling the sight-box provides a view, and samples may be run off from the gauge-glass. The product, after passing through the mill, runs off continuously from the base outlet.

In some cases it is not considered economic to aim at a complete disintegration of the material in one set of millings, but to allow the non-colloidal material to settle out for milling in a succeeding batch.

If the milling continues over several minutes, a rise in temperature takes place. In the majority of cases this heat is stated to assist disintegration, but sometimes it is a disadvantage which must be obviated by a flow of water through cooling coils in the upper part of the machine. In some cases the injection of steam into the machine facilitates the disintegration.

Thus, a Plauson-mill installation would usually include preliminary crushers or breakers, pre-grinding mills, sieves, storage and mixing tanks for water, accelerator and suspension, and settling tanks for the milled

product together with elevators, conveyors and dust catchers. When the colloid has to be separated special filters and driers might also be required (E.P. 155,834).

The output and power consumption of the mill depend on the ease of disintegration of the material, the extent of disintegration, and the rate of revolution of the mill. It is stated that three 15-litre machines in series, running at 9,000 r.p.m., can grind 1,000 kg. ground 'raw phosphate', or 200 kg. cellulose in an hour to such a state of division that 85 per cent of the particles is estimated to be of the order of 0·001 mm. diameter. With the new machines, fitted with baffles, &c., and possibly run at higher speeds, a much greater output per h.p. is claimed.

For convenience the industrial uses claimed for the colloid mill have been divided into four groups.[1] The following is a brief outline, under these headings, of some of its uses :

I. THE PREPARATION OF PLASTIC MASSES

Raw material	Use
Sawdust-waste, wood-meal, mica waste (with resin, &c.)	Insulators, buttons, &c.
China clay	Filling, &c.
Rubber waste	Regeneration and moulding
Gelatin, casein, starch	Masses

II. THE PREPARATION OF COLLOIDAL SOLUTIONS FOR DIRECT USE

Raw material	Use	Remarks
Sulphur	Disinfectant, spraying on plants	Rapidly absorbed
Creosote	Do., general	Avoids precipitation by dilution
Metals Cu	} —	—
Mn		
Ag		
Phosphate	} Fertilizers.	{ Rapidly absorbed without sulphuric-acid treatment
Felspar		
Milk (condensed)	Formation of milk (substitute)	—
Tar	Road spraying, &c.	Saves heating
Scents	} Scents	{ Saves solvent for exporting abroad. Increased efficiency
Essential oils		
Mineral and organic pigments	Inks	New pigments can be used
Graphite	} Lubricants	{ Enhanced lubrication, avoids overheating of lubricant and charring
Oil (grease)		
Water emulsion		
Resin (in water)	Polishes	Saves solvent
Vaselines	—	—
Shellac	Lacs.	Saves solvent
Resin, size, cellulose esters, copal, Bakelite, rubber	Enamels, &c.	—
Ultramarine	Paints, &c.	—
Metals and alloys (bronze)	Paints, &c.	—

[1] Forster and Reilly, *J. Soc. Chem. Ind.*, 1922, *41*, 20.

III. THE DIVISION OF MATERIALS FOR CHEMICAL ACTION

Raw materials	Use	Remarks
Fats	Soap . . .	Cold saponification
Nitro-compounds . .	Dyes, &c. . .	Cold reduction to amino-compounds
Nickel	For hardening oils .	—
Cellulose	⎰Fermentation . .	Rapidly assimilated
	⎱Viscose . . .	Reduces amount of reagents

IV. THE SEPARATION OF MIXTURES BY FRACTIONAL DISINTEGRATION

By suitably adjusting the speed of the mill and the type and amount of accelerator, intimate mixtures are fractionally disintegrated; and if the milling be suitably timed, a separation of one ingredient in colloidal solution from another in coarse suspension by simple screening through fine mesh sieves can be made.

(b) **Chemico-mechanical.** Combined chemical and mechanical methods are more common than purely mechanical. A colloid which has been precipitated by one electrolyte may, in some cases, return into apparent solution when the excess of the latter has been washed away. If a silver halide precipitate is washed immediately, the silver may go into colloidal solution when the excess of the electrolyte is removed. Colloidal zinc sulphide may be obtained by washing the hydrogen sulphide precipitate from an ammoniacal zinc solution with pure water. Precipitated copper ferrocyanide will do the same when the copper sulphate has been washed away. A phenomenon used in the preparation of colloids is that of peptization. This is a dispersion of the precipitate by the action on it of an electrolyte. Graham peptized silicic acid by means of caustic soda, and Prussian blue may be peptized by oxalic acid. Cadmium sulphide sol may be prepared in this manner. The sulphide is first precipitated by passing hydrogen sulphide into an ammoniacal solution of cadmium sulphate; the liquid is decanted from the precipitate, thoroughly washed and suspended in water. Hydrogen is now passed through the suspension, and after some time the liquid becomes milky and finally perfectly translucent, a golden yellow sol resulting. Another peptization method has been developed and patented by Kuzel for preparing sols of a large number of heavy metals. The metal is first ground to an extremely fine degree and then treated alternately with dilute acid, water, and dilute alkali; after a number of such treatments the metal disperses spontaneously in distilled water.

(c) **Electrical Methods.** Of electrical methods of preparation that of Bredig is best known. This consists in the formation of a direct-current arc under water, using the metal as electrodes (Fig. 2 (V *)). The latter is disintegrated and colloidal solutions result. From 30 to 40 volts and 5 to 10 amperes may be used. A trace of alkali in the water is advisable, to stabilize the resulting colloid. The method has been improved by Svedberg, who uses an oscillatory discharge from an induction coil with a condenser in circuit. A large capacity, small self-induction, low resistance and short arc were found to give the best results. Svedberg thus prepared colloidal solutions of all the metals. Organic dispersion media were used as well as

water. Morris Airy and Long use a high-frequency alternating arc, a suitable generator being provided by the Poulsen arc as used in wireless telegraphy. The discharge circuit contains an arc lamp, designed to allow the arc to be struck under water. By varying the inductance and capacity of the oscillatory circuit and introducing various capacities and inductances into the discharge circuit, the conditions of the discharge can be varied between wide limits. A few minutes are generally sufficient to prepare solutions of the metals. By varying the conditions of discharge it has been found that differently coloured solutions of the same metal may be obtained.
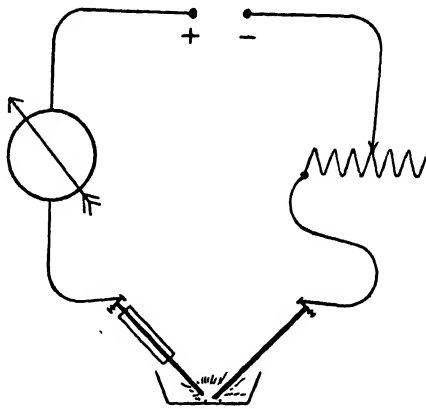
FIG. 2 (V *)

Emulsoids. The preparations just described are used mainly for the production of inorganic suspensoid sols. The investigation of these has been more fruitful from the theoretical aspect than that of the organic colloids. The latter, however, are very numerous, forming the vast majority of the class of sols known as *emulsoids*. They are extremely important, as they include most of the proteins, a number of carbohydrates, the soaps, &c.

Preparation Methods. The preparation of dilute emulsions may be accomplished in some cases by agitation of the mixed phases. Oil and water, when shaken together, will produce a temporary emulsion, but after a little time the drops coalesce. If the concentration of the oil is very low, a stable emulsion may be formed. White of egg mixed with water forms a clear emulsoid slightly opalescent. Agar and gelatin disperse in water on heating, forming emulsoid sols. In general, however, to prepare a stable concentrated emulsion a third substance, the emulsifying agent, must be present. This third substance is, very often, also colloidal in solution.

Emulsifying Agents. Gelatin is much used as an emulsifying agent. Benzene may be emulsified in water by means of gelatin; albumins, gums, dextrin, starch, casein, haemoglobin, pepsin, peptone, &c., have all served as emulsifying agents. Soaps are excellent emulsifiers for all kinds of oils and fats. Pickering's investigations in this direction have become classical. 99 ml. of paraffin or benzene have been dispersed in 1 ml. of water by means of soap as emulsifying agent. Fine'y divided solids are also used as emulsifying agents. Pickering has shown that the basic sulphates of iron, copper, nickel, zinc, and aluminium may be used in dispersing mineral oil in water. Lampblack may be used to disperse water in kerosene.

Dialysis. The colloidal sols prepared by most of the methods described, contain, owing to the methods of their preparation, some quantity of crystalloids. The colloidal and crystalloidal particles are separated by dialysis. This is a process of diffusion through a membrane porous to

substances in true solution, but impervious to the colloidal aggregates. The mixed colloid and crystalloid is placed at one side of the membrane and the pure dispersion medium at the other. The crystalloids tend to have the same concentration on both sides of the membrane and therefore diffuse through to the pure liquid. Prolonged dialysis with frequent changes of liquid outside the membrane results eventually in complete separation of the colloid and crystalloid.

Dialysers. The usual membranes used in dialysis are gold-beater's skin (the peritoneal membranes of cattle), collodion membranes, parchment paper, and fish-bladder. The speed of the dialysis largely depends on the surface of the membrane in contact with the liquids. Holmes describes an easily made dialyser with a large working surface. This is a sheet of parchment paper shaped like a beaker. The sheet of parchment, free from pinholes, is soaked in water for a few minutes to soften it and then folded over a bottle of the desired size and shape. The folds should be triangular and narrow and cover one another like the folds of an umbrella. A cord is tied around the paper and bottle about 1 cm. from the upper edge, and the whole set aside to dry. The bottle is then removed and the parchment keeps its shape. So tough is the paper that a parchment cup holding a litre of water may be carried without tearing or collapsing. The dialyser is nearly filled with the colloidal solution and suspended in a large vessel of pure water (Fig. 3 (V *)). The rate of dialysis is very rapid. A double surface may be used by suspending a smaller parchment shape containing pure water inside the shape holding the colloid. Greater dialysing rapidity may be obtained by having a constant flow of pure water outside the parchment membrane.
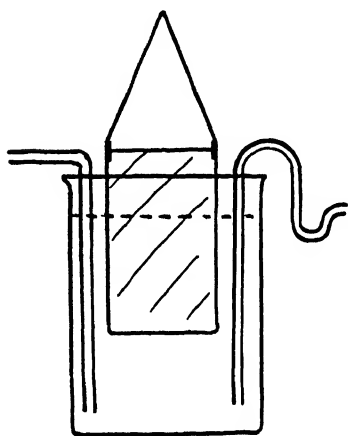
FIG. 3 (V *)

Electro-Dialysis. This process is useful for the removal of mineral matter from natural products. In the electro-dialyser devised by Reilly and McSweeney[1] two concentric cylinders are employed (Fig. 4 (V *)). These are closed at the bottom with parchment and immersed in water in a large outer vessel. Simple collodion, albumin collodion or other membranes may be employed. Tubular forms of viscose known as cellophane, which are now cheaply obtained, may also be employed with advantage. The glass cylinders in the dialysing apparatus are made in sizes to suit the volume of liquid to be dialysed.

Water is circulated in the outer vessel and the inner cylinder by means of a siphon arrangement, indicated in the figure. Platinum electrodes are placed below the outer membrane and above the inner one. Nickel gauze, copper gauze, silver, and gold have also been suggested as electrodes in the literature.

The substance for dialysis was dissolved in distilled water at a con-

[1] *Sci. Proc. Roy. Dub. Soc.,* 1930, *19,* 38.

venient and arbitrary concentration, and the solution placed in the annular space between the cylinders.   In a series of experiments carried out with this apparatus a difference of potential of about 230 volts (taken from the D.C. mains) was applied to the electrodes, and the current passed through for a period of from 6 to 12 hours.   The solution was agitated by means of a glass stirrer, which encircled the inner cylinder, and was raised and
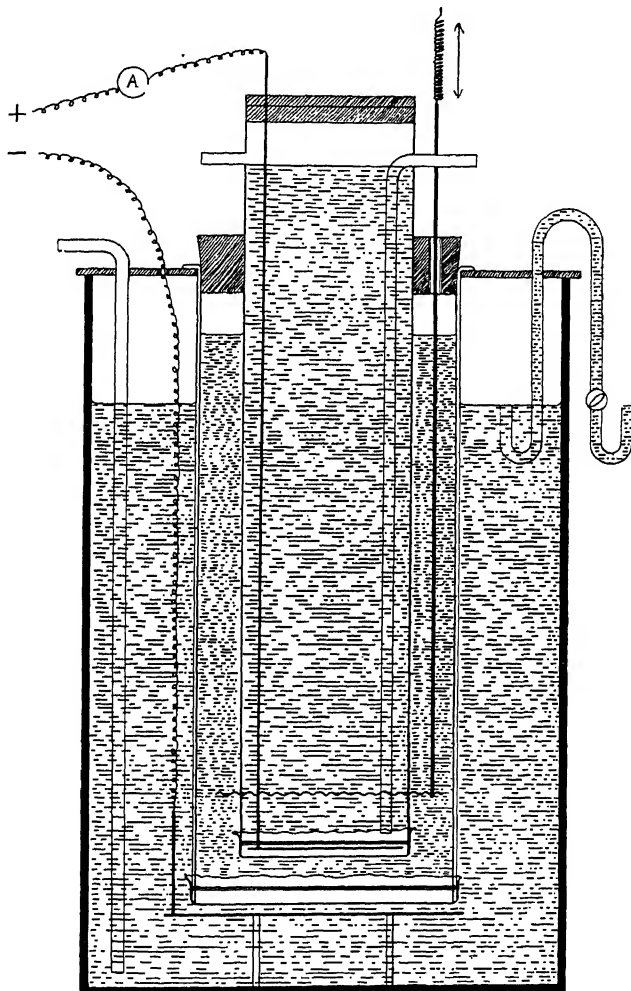
FIG. 4 (V*)

lowered by a mechanical arrangement.   The membranes were kept at a distance of 4 to 5 cm. apart.   The electrodes were kept as near as possible to the membranes without actually touching them.   During the last hour of the dialysis the water in the inner cylinder and outer vessel was replaced by distilled water.

With this apparatus the ash content of crude manna, inulin or glycogen can be readily reduced to very small amounts.

Collodion Membranes. Collodion dialysers are much used in colloid work. Collodion solution is prepared by pouring 75 ml. of ethyl ether over 3 grams of commercial pyroxylin in a flask, corked to prevent evaporation. After 10 or 15 minutes 25 ml. of ethyl alcohol are added. The pyroxylin quickly changes to a clear solution. Other proportions of solvent and solute may be used for particular purposes. The method of Noüy is the most convenient one for making the tubes. A small orifice 1 or 2 mm. in diameter is blown in the bottom of a tube of the diameter of the collodion sac required. This hole is first closed by a layer or two of collodion, care being taken not to allow any to go inside the tube. A flask or cylinder containing the collodion solution is tilted to allow this tube to roll inside it in the solution. The tube thus coated with collodion is removed and some of the solvent allowed to evaporate. It is then inserted in the flask and rotated once more to give it a second coat and the operation repeated till the collodion is of any desired thickness. When the coating has 'set' and does not stick to the finger, the tube is plunged into water and water also poured into the interior. If the immersion in water is made too soon, the collodion becomes opaque and brittle; if too late there may be difficulty in removing it from the tube. The proper interval must be learned by trial. By blowing into the tube the water is forced through the perforation in the space between the coating and the glass; the membrane may then be removed by pulling and twisting. Dialysis occurs with great rapidity through these sacs and the whole process may be watched owing to their transparency. The dialysing power of such membranes have been compared with that of parchment and gold-beater's skin; the latter is found to be most suitable, and the parchment least suitable. Collodion membranes made as above are found to be lacking in uniformity both as to thickness and dialysing power. Walpole[1] prepared films by allowing a measured quantity of collodion solution containing a known amount of gun-cotton to evaporate on a known area of glass plate. In this way flat membranes were obtained with definite and uniform characteristics respective to strength and permeability. They can be affixed to wide-mouthed bottles by collodion around the rim. Farmer[2] describes an apparatus for making collodion tubes in which all variables except the time of drying are fixed.

HOT DIALYSIS

FIG. 5 (V *)

Hot Dialysis. The speed of dialysis may be largely increased by rise of temperature. A simple hot dialyser has been described by Neidle.[3] The method consists in suspending a parchment paper membrane of about 1 litre capacity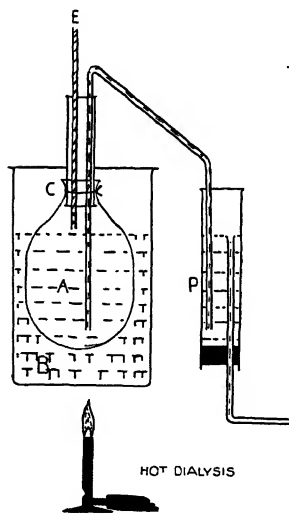 in a 2-litre beaker containing about a litre of the solution to be dialysed (Fig. 5 (V *)). Distilled water is run at a fairly constant rate into a mem-

[1] *Biochem. J.*, 1915, *9*, 284.   [2] *J. Biol. Chem.*, 1917, *32*, 447.
[3] *J. Amer. Chem. Soc.*, 1916, *38*, 1270.

brane which is maintained a little more than half full by means of an automatic siphon. The colloidal solution which is in the beaker is heated to any desired temperature (70° to 90°). The diffusion coefficient of the electrolyte increases about 2 per cent per degree, so a rise of from 50° to 70° has a very appreciable effect.

A colloidal solution of high purity may be obtained by this method in 8 to 10 days, while the usual method may require a month.

Dialysis. The electrodialysis Cenco-Loddesol apparatus [1,2,] is very suitable for the electrodialysis of colloidal materials and the fractional electrodialysis of soil suspensions in distilled water and other determinations.

The advantages of the electrodialysis method over the neutral salt extraction method are, greater rapidity of determination, elimination of the solvent effect of the reagent, and greater simplicity in the analysis of the dialysates. While this apparatus was devised especially for soil investigations, it is well adapted to many other investigations in physiological and electro-chemistry where colloids are to be purified, membrane potentials are to be determined, &c.

The apparatus consists of an assembly of five glass cells separated by membranes, rubber gaskets with two platinum rhodium electrodes of large area between the cells of each end of the group. These are held rigidly in place by a compression screw clamp and are supported by adjustable brackets upon a substantial japanned and nickel-plated iron support. The support is provided with electrical connexions for the electrodes, a support rod for the stirring motor, a water-spray for cooling the central compartment and a water-drain unit for removal of the cooling liquid. Each cell has a top opening for introduction of water and is provided, in the case of the outer cells, with rubber tubing outlets closed by pinch clamps from which samples may be withdrawn. The central compartment has a large bore glass stopcock through which the soil suspension is easily withdrawn.

The shape of the central compartment or cell is globular to provide a large capacity within as short a distance as possible between the flanges, to keep the internal resistance of the entire assembly at a minimum value. The globular shape also permits more effective stirring of the soil suspension than would be possible with a tubular cell. Plain cellophane, waterproofed cellophane, animal and vegetable parchment sheets are provided to permit the use of the membrane best adapted to the work at hand in the assembly of the apparatus. [3]

Ultra-filtration. The process of ultra-filtration developed by Bechhold resembles the process of dialysis. The membranes used are similar to the collodion membranes described. The membrane is not, however, submerged in the pure dispersion medium. The process consists in forcing the solution through the membrane under pressure. Particles too large to pass through remain behind while smaller particles are not impeded. By the use of membranes of different porosity, colloids of different sizes may be separated, and from determinations of the pores of the filter the

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[1] Pat. No. 1,926591. Made by the Central Scientific Co., N.Y.

[2] Dr. Aasulv Loddesol, 'A New Modification of the Three-Compartment Electrodialysis Apparatus', *J. Amer. Soc. Agron.*, 24, 74–81, and *Soil Science*, 33, 187–211.

[3] See also Hixon and Martin Electrodialyzer for Starch, *Ind. and Eng. Chem. Anal.*, 1939, *11*, 395.

approximate size of the particles may be deduced.   To permit the use of pressure the membranes are prepared as follows : Strong, hard filter paper is impregnated, preferably *in vacuo*, with either a gelatin sol or an acetic acid collodion solution of known concentration.   In the case of gelatin the filters are then immersed in cold formaldehyde for several days ; the collodion films are immersed in water, which replaces the acetic acid and leaves the paper choked with a gelatinous mass of cellulose.   The porosity of the filters may be varied by altering the concentration of the original gelatin or collodion, so that a series of filters of increasing porosity can be prepared.   When in use the filters are supported on fine wire gauze or perforated metal, so pressures up to ten atmospheres may be used.   The pressures originally used were from two to ten atmospheres.   In one form of the filtering apparatus a stirrer was used to keep the particles violently agitated.   (See chapter on Filtration, IV *, S. 3.)

Size of Pores.   In determining the approximate size of the pores two methods have been used : treating the filter as a collection of capillary tubes, their dimensions may be arrived at by determining the pressure required to force air through them when immersed in water, or the volume of water forced through a known area in a given time, under a known pressure, may be measured.   Bechhold used ox-blood particles of known diameter as a test of the method.   Hatschek has indicated a method of measurement by determining the pressure at which oil globules of known size, suspended in water, are just forced through the membrane.   The inter-facial tension oil/water being known, the radius of the pores—assumed to be of circular section—can be calculated.

Ultra-microscope.   When an intense beam of light is projected

FIG. 6 (V *)

through a colloidal solution, the path of the beam, viewed at right angles to the direction of propagation, is clearly visible.   With a crystalloid solution free from impurities no such effect is apparent. The phenomenon was noticed by Faraday in his gold sols and was subsequently used by Tyndall.   It is generally referred to as the *Tyndall effect*.   The effect is apparently due to light scattered by the individual colloid particles, and the idea of isolating the reflections from the individual particles has been developed.

The instrument for this purpose is known as the ultra-microscope (Fig. 6 (V *)).   A powerful beam of light is thrown horizontally through a cell containing the liquid and the illuminated portion is observed through a microscope, the axis of which is vertical and thus at right angles to the beam.   No light must be allowed to enter the microscope directly.   With proper magnification the colloid particles are seen as bright
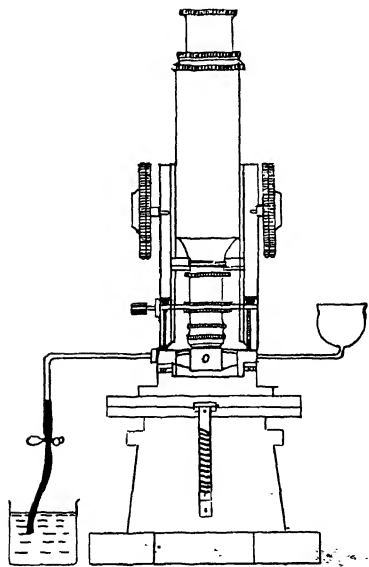
discs on a dark background. Their visibility depends upon the intrinsic brilliancy of the beam, the size of the particles, and the optical difference between the particles and the surrounding medium. Inorganic colloids are generally good subjects for the ultra-microscope, but many organic colloids, e.g. solutions of proteins, do not show individual discs of light, but a general diffused light is observed. This is probably due to similarity in optical properties of the disperse phase and the dispersal medium.

Working Method. The usual setting of the ultra-microscopic apparatus is as shown (Fig. 7 (V *)). The light of a powerful arc lamp is projected
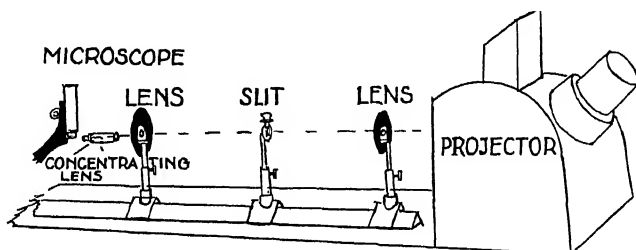
FIG. 7 (V *)

by a lens on a ' precision ' slit. An image of the slit is formed by the second lens and projected on the illuminating device, which is similar to a microscope objective. This directs the beam through a cell containing the liquid on a platform of the microscope. The microscope is then focused on the liquid.

Size of Particles. The ultra-microscope may be used to determine the size of colloid particles ; the major portion of the illuminated volume can be cut off and the length and width of the residual part measured by means of an eyepiece micrometer. The slit can then be turned $90°$, so that the depth may be measured. The average number of particles in this known volume is determined by repeated counts ; the weight of colloid per unit volume may be obtained during its preparation. Assuming then that the density of the particles is the same as when in bulk and that the particles have a simple geometrical shape, the order of magnitude of the particles can be calculated.

Paraboloid Condenser. Where exact observations are not needed, the optical examination of colloidal solutions may be performed by a Zeiss paraboloid condenser. This is a much less elaborate instrument. A section of the condenser is shown (Fig. 8 (V*)). Parallel rays entering the condenser axially are reflected to the focus of the paraboloid ; this is arranged to be on the plane top surface of the condenser ; a central stop covers part of the bottom face, so that only those rays will pass which will, after reflection, be totally reflected by the top of the condenser, if in contact with air. Cedar
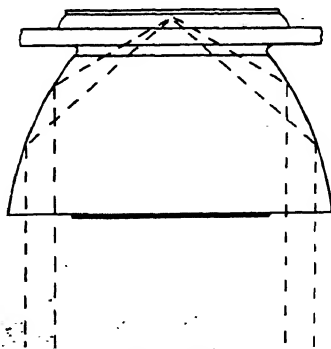
FIG. 8 (V *)

oil between this surface and the slide containing the colloid allows the rays to pass through the latter; these, however, are totally reflected at the cover-glass which rests on the solution. No direct light, therefore, enters the microscope, but light dispersed by the colloid particles can be brought to a focus.

Jentsch Condenser. Another form of condenser, the Jentsch ultra-condenser, avoids the use of slides and cover-glasses. A section of the condenser is shown (Fig. 9 (V *)). The liquid is placed in the spherical hollow, which is closed by a quartz cover and holds about 1 ml. The lower face of the condenser is provided with a central stop. The rays which enter are twice reflected as shown by the dotted lines, and come to a focus in the axis at some point near the top of the cavity. A thin layer of the liquid is thus intensely illuminated and no direct light passes axially. The field may then be viewed through a microscope.
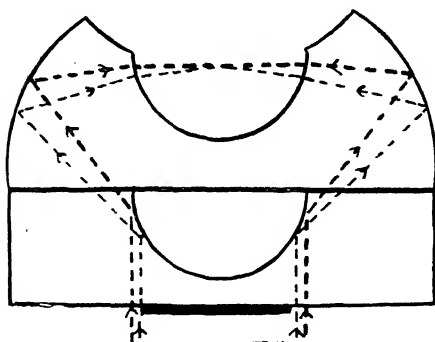
FIG. 9 (V *)

Brownian Motion. Observations on microscopic and ultra-microscopic particles suspended in a liquid have revealed a peculiar trembling motion of the particles; each particle executes an erratic translatory motion about a mean position; the smaller the particle the more violent the motion. The hypothesis that the m~~~~ ~~ ~~~ ~~ ~~~~~~~~~ ~~~~~~~~ has been put forward, and from investigations on this basis the kinetic theory of matter has received direct experimental verification. Though the phenomenon is apparent with microscopic particles, the important work in the subject has been accomplished with the use of the ultra-microscope.

Velocity Measurements. Measurements of the velocity of such particles have been made by a number of workers. The first measurements were made with microscopic particles, by means of a micrometrically divided scale. Later a photographic method, taking photographs at intervals of

FIG. 10 (V *)

0·05 second was used. The position of a given particle on squared paper was marked according to scale at intervals of thirty seconds, following one particle for long periods (Fig. 10 (V *)). Svedberg modified the appearance of the motion by giving the liquid a translatory motion (Fig. 11 (V *)); this was accomplished by allowing a slow current of the colloid to flow through the cell during the observation. The velocities
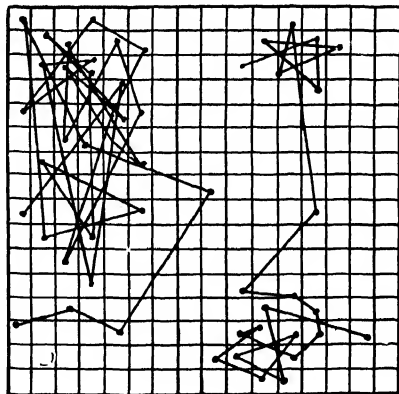
observed by these experimenters have been of the same order as those calculated by Einstein, Smoluchovski, and Langevin.

Perrin's Investigations. Probably the most outstanding contribution to the kinetic theory of the motion is that of Perrin. Perrin extended the gas laws to the case of colloidal particles, so that a colloidal particle agitated by the Brownian motion would count as an ordinary molecule, with respect to its effect on impact with a partition that stops it. On this basis the law of distribution of the molecules of a gas according to height should hold also for a colloidal solution. A small elevation h in a colloid should therefore change the concentration of the particles from n to n^1 according to the equation :

FIG. 11 (V*)

$$\frac{n^1}{n} = 1 - \frac{N}{RT}m\left(1 - \frac{d}{D}\right)gh$$

N = Avogadro's constant (the number of molecules per gram. mol.)
R = gas constant
T = absolute temperature
m = mass of a particle
D = density of colloidal material
d = density of the liquid
g = acceleration due to gravity

The first requisite to test the equation is a colloid the particles of which are of uniform size. Perrin accomplished this by a process of fractional centrifuging of the colloid. The solutions used were gamboge or mastic dispersed in water ; these are prepared by dissolving the solid in alcohol and adding much water.

Density of Particles. To determine the density of the colloid material three methods were used :

(a) By the specific gravity bottle, as for an insoluble powder.

(b) Drying the colloid at 110° gives a glass-like solid. This is placed in water, to which is added sufficient potassium bromide to cause the fragments to remain suspended without rising or sinking ; the density of the solution is then found.

(c) By adding potassium bromide to the emulsion until on energetic centrifuging the grains neither rise nor sink ; the density of the liquid is then obtained. By these three methods the same gamboge grains gave the values 1·1942, 1·194, 1·195.

Sedimentation Test. Ostwald and von Hahn [1] measured approximately the rate of settling of particles. Their method depends on the fact that a suspension is specifically heavier than the medium and hence if the suspension is placed in one arm of a U-tube and the suspension
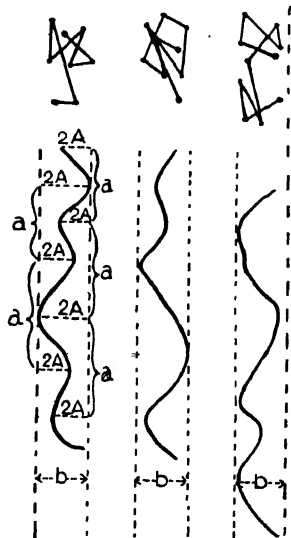
[1] *Kolloid-Z.*, 1923, *32*, 60.

medium in the other, the latter will stand at a higher level. As the solid settles out the suspension becomes specifically lighter and the level difference of the two arms decreases. From the rate at which the level difference decreases a rough idea of the rate of settling can be obtained. Von Hahn's [1] tube is shown in Fig. 12 (V *). In Kelly's modification (Fig. 13 (V *)) much more dilute suspension may be employed, 0·5 to 1 per cent against 20 per cent. The actual weight of material settling past the entrance of the side-tube can be measured.
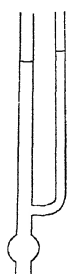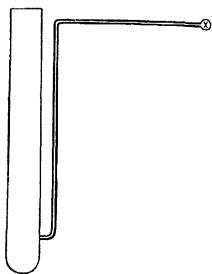
Volume of Grains. (a) A drop of

FIG. 12 (V *)

FIG. 13 (V *)

very dilute emulsion is allowed to evaporate on an object-glass. The grains run together and arrange themselves in rows. Microscopic measurements of length of a number of grains are then possible.

(b) *Weighing the Grains.* Allowing the grains in a given solution to adhere to the wall of the microscopic slide, and counting them at leisure, the weight of all the grains in a given volume is found by evaporation and weighing. The weight of one grain is thus obtained.

(c) By observations of the rate of fall of one particle in the liquid and applying Stokes' Law. (See Chapter XII, S. 7.)

Relation between $\dfrac{n^1}{n}$ **and** h. A cylindrical column of height 0·1 mm. was viewed with a microscope which could be focused at different heights on the liquid (Fig. 14 (V *)). The distribution reaches a steady state and
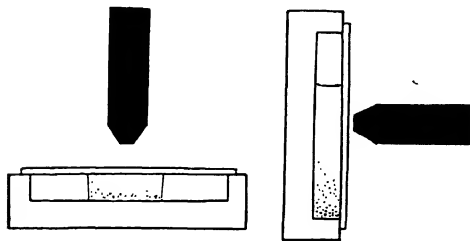
FIG. 14 (V *)

the particles all remain in suspension. The number of particles visible at heights differing by 30μ were counted (Fig. 15 (V *)). The proportions counted at heights 5μ, 35μ, 65μ, 95μ were 100, 47, 22·6, 12. These are approximately equal to the numbers 100, 48, 23, 11·1, which are in geometrical progression.

By these methods Perrin obtained a value for N agreeing with that found by totally different methods ; the value was constant, however the conditions of the experiment were varied.

Electrical Properties. The possession of an electric charge by the colloidal particle is a remarkable property of most colloidal solutions; this property is extremely important in the theory of colloids, forming as it does the basis of the explanation of some fundamental colloid peculiarities. The investigation of this property dates from the work of Linder

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[1] *Ind. and Eng. Chem.*, 1924, *16*, 928.

and Picton.   Prior to that, experiments on the motion of the particles of ordinary suspensions under an electric field carried out by various workers, had led to the general conclusion that ' in water all bodies appear, through contact, to become negatively charged, while, through rubbing against various bodies, the water becomes positively charged '.   Linder and Picton disproved the truth of this statement and showed that the charge on the suspension is more nearly related to the acidity or basicity of the solution.

Velocity in Electric Field. U-tube Method. For the observation and measurement of the migration of the colloid particle in an electric field, we may observe either the motion of the solution as a whole or that of individual particles, under the ultra-microscope. The first method was used by Hardy, Burton and others, and is probably the more reliable of the two. The velocity tube was of the form shown (Fig. 16 (V *)). It consists of a U-tube each limb of which may be 12 cm. long and 1·5 cm. in diameter ; the limbs may be graduated in millimetres through-out their length. Into the bottom of the U-tube is sealed a fine delivery tube provided with a tap T, and funnel F. This tube is bent round behind the limbs and the funnel is the same height as the top of the U-tube.
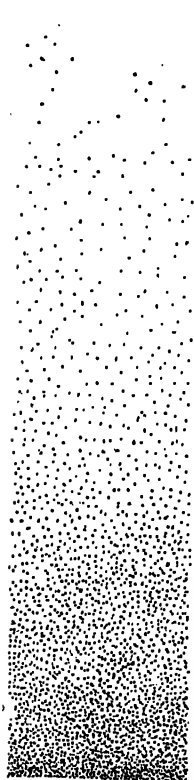
The colloidal solution to be tested is poured into the funnel, so as to fill the small tube and funnel round to the tap, which is closed ; water having a specific conductivity equal to that of the colloid is then poured into the U-tube so as to fill it to a height of about 3 cm. The whole tube is then placed in a glass water-

FIG. 15 (V *)
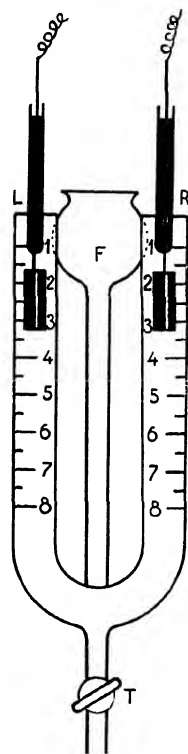
FIG. 16 (V *)

bath of constant temperature. At the end of a few minutes the tap T is slightly opened and the colloidal solution allowed gently to force the water up the limbs of the tube to any required height. With careful manipulation the surface of separation between the clear water and the colloid can be made very sharp ; the success of the experiment is dependent on this manipulation. Two electrodes of platinum foil are supported at a convenient level in the two limbs of the tube. These are attached to the terminals of a set of storage cells of constant voltage ; a reversing key should be included in the circuit. The circuit may be made in one direction for 10 minutes and then reversed for 20 minutes ; the

measurement is made during the latter period. Each surface displacement is measured and the total halved. The motion of the surfaces may be measured directly or by means of a cathetometer.

Strength of Field. To determine the value of the electric force in the tube, it is necessary to know the effective distance between the bottom ends of the two electrodes. This is accomplished by filling the tube with a 0·01 N. KCl solution. It is placed in the water-bath, and the resistances taken with the electrodes placed at the successive centimetre marks in the tube. In this way the resistance of the curved part of the tube compared to each centimetre length is found. The distance between the electrodes and the velocity per unit potential gradient are then calculated. A typical set of observations is given by Burton.

Time.	Voltage sign of electrode L	Temp.	Height of colloidal surface		Observed Vel. in cm./sec.
			Left	Right	
11·37	+ 118	11°	54 mm.	55 mm.	
11·47	+ 118		61 mm.	50 mm.	
Current off					
11·48	− 118	11°	61 mm.	50 mm.	
11·58	− 118		55 mm.	56 mm.	96 × 10⁻⁵
12·08	− 118	11°	50 mm.	62 mm.	

The strength of the field was 4·9 volts per cm. Thus the absolute velocity of the colloid particles was $19·6 \times 10^{-5}$ cm. per sec. per volt cm.

Microscopic Method. The ultra-microscope was first used for velocity measurements by Cotton and Mouton. The solution was placed on a microscope slide ; two electrodes were introduced a few millimetres apart and a difference of potential of a few volts established (Fig. 17 (V *)). The time required for a single particle to cross the field of view was then noted. The walls of the slide cavity were found to reverse the motion of the particles near them, but the motion in the body of the liquid was normal.
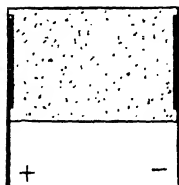
FIG. 17 (V *)

Electrical Osmosis. This latter phenomenon (the reversal of motion near the walls of the vessel), is a particular instance of a general phenomenon known as *Electrical Osmosis*. When the anodic and cathodic compartments of a conductivity tube are separated by a porous medium, the electrolyte will pass through the pores of the medium towards the cathode until equilibrium is established. Quincke noticed a similar effect when using capillary tubes instead of a diaphragm. The phenomenon is not directly a colloidal one, but it is linked with colloidal phenomena since the same theory of electric charge—a condenser-like surface double layer—is applied. In cataphoresis the surface holding the double layer is free to move and cause movement of the colloid particle, in electrical osmosis the surface is fixed and the liquid moves. Perrin has investigated the phe-

nomenon for a number of liquids. The demonstration of this phenomenon can be very simply accomplished (Fig. 18 (V *)).

A circular porcelain diaphragm is sealed in the centre of a wide tube with Canada balsam. The tube is closed by two tight-fitting corks, to which run leads to two electrodes inside the corks. Each compartment
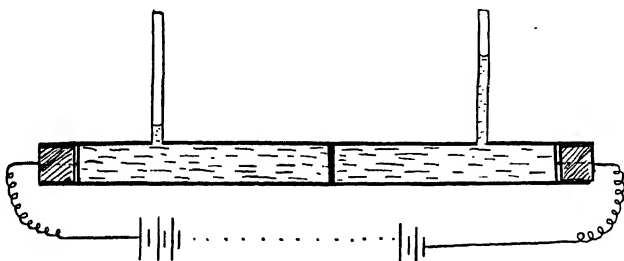
FIG. 18 (V *)

of the tube is fitted with the experimental liquid, the level being equal in the two upright tubes. When the voltage is applied, the liquid level will fall in one tube and rise correspondingly in the other.

Coagulation of Colloids. Graham, in his first discussion of colloids and crystalloids, has noted the fact that colloids are generally displaced or precipitated from solution by the addition of any substance from the other class (e.g. crystalloids). Faraday noticed that his chemically prepared gold solutions changed colour on the addition of salt and ascribed the change to an increase in the size of the aggregates. Jevons noticed that the addition of acids, alkalis, or salts to suspensoids caused the cessation of the Brownian movement of the particles. That suspensoid sols are extremely sensitive to small quantities of electrolytes is now generally known; emulsoid sols are different in this respect, large concentrations of electrolytes being usually necessary for precipitation. Comparatively little work of this nature on the latter class has been accomplished; the suspensoid sols have presented a more attractive field from both the practical and theoretical standpoints.

Quantitative Measurements. Schulze investigated the properties of arsenious sulphide and antimony sulphide sols. The coagulative powers of different salt solutions were tried; he came to the conclusion that the coagulative power depended solely on the metallic ion and not at all on the acid radical. Linder and Picton have performed experiments of the same nature with arsenious sulphide. They found that metallic salts arrange themselves in sharply divided groups as regards their power of aggregating this solution. This power is dependent on the valency of the metal; thus tervalent metals have the highest coagulating power, bivalent metals about one-tenth of this, and univalent metals less than a five-hundredth. These authors also examined the relation between the coagulative power and the ionic dissociation of salts of the same metal. The constants were found to be approximately proportional.

Velocity in presence of Electrolytes. The results, taken in conjunction with the charged nature of the colloid particle, lead to the assump-

tion that coagulation depends on the neutralization of the electric charge. This was first suggested by Jevons. Burton carried out experiments on the effect of electrolytic solutions on the mobility of colloids in an electric field; the U-tube apparatus previously described was used. Metallic sols prepared by Bredig's method were experimented with. Solutions of salts of determined normality were prepared with conductivity water and the amount of such solution added to a given quantity of colloid solution was measured by counting the drops as they came from a fine burette. The velocity of the precipitation in the pure copper solution was first taken, gradually increasing quantities of the chosen electrolytic solution were then added to fresh colloid, and the velocity measured each time. The velocity was found to decrease as the quantity of negative ion increased, and the decrease in the velocity depended on the valency. The particles were found to coagulate when they ceased to move in the field, i.e. when they had lost their charge. This work, therefore, confirms the previous work of Schulze and Linder and Picton as well as verifying the above hypothesis of Jevons.

Mutual Precipitation. The electrical nature of coagulation is further confirmed by the fact that colloids of opposite electric charge (as determined by cataphoresis) exert a mutual precipitating action. The phenomenon occurs only within certain cencentration limits; the result is not achieved with too dilute or too concentrated sols. The precipitate obtained is a close mixture of the two colloidal substances.

Viscosity. With suspended sols the determination of viscosity has not shown any marked anomalies, the values obtained not differing materially from that of the pure dispersion medium. With emulsoid sols this coefficient has been found to increase very rapidly with increase in disperse phase, and the temperature coefficient is much greater than for the dispersion medium. The coefficient has been found to decrease very rapidly with rate of shear. On this account methods allowing direct variations in the rate of shear are more popular. Garrett used the logarithmic decrement of an oscillating disc, and Hatschek used the torque of concentric cylinders one of which is rotated with a constant velocity. The ordinary capillary-tube method has also been used.

Surface Tension. For the methods of determination of this value see a previous chapter. Owing to the fine state of subdivision of the material, surface effects play a fundamental part in colloidal questions. The very important phenomenon of adsorption is a surface effect and its action has been much felt in colloidal problems.

Adsorption. The capacity of charcoal to condense large quantities of gases has been used to attain high vacua, and to separate gaseous mixtures; its properties as a filtering medium for removing colouring matters from solution are used industrially. Other porous substances such as china clay and fuller's earth have the same power to a greater or less degree. That these properties depend on the large exposed surface of these materials appears an acceptable hypothesis. It appears that every surface tends to attract every other substance more or less. The exact nature of the union is not definite : the adsorbed substance is not held by a chemical bond in the ordinary sense ; the adsorption may be said to be due to free surface

forces. It may be considered as a concentration of dissolved or dispersed substance upon the solid, liquid, or gaseous adsorbing surface. This subject is treated in the next section.

Adsorption by Precipitates. When barium sulphate is precipitated from a strongly alkaline solution of potassium permanganate, the precipitate remains red; the adsorbed permanganate cannot be removed by washing or even by hydrogen peroxide.[1] This precipitate generally is marked by great adsorbing power. In precipitating with barium chloride, hydrochloric acid is adsorbed, and the precipitate weighs too heavy. On heating, the hydrochloric acid is driven off. Patten shows that barium sulphate adsorbs salts of nickel, cobalt, chromium, iron, and manganese. Many metallic salts in solution are adsorbed by the fibres of the filter paper during filtration. A change in concentration on filtering is thus noticed.

Capillary Analysis. The different power of adsorption of filter paper for different salts in solution points to a method of capillary analysis. To a dilute solution of copper and cadmium sulphate add ammonia till alkaline and dilute largely. Allow several drops to fall on the centre of a piece of filter paper and hold the paper over a bottle of ammonium sulphide. Three rings appear—an outer water ring, a yellow cadmium ring, and a central black ring of copper and cadmium. The more powerful adsorption of the copper causes the separation.

Gibbs' Equation. The thermodynamically derived equation of Willard Gibbs is regarded as fundamental to the problem of adsorption. Gibbs' theory is based on the tendency of surface energy to assume a minimum value and the fact that an increased concentration in the surface layer leads to a reduction of the surface tension. He arrived at the following expression :

$$U = -\frac{C}{RT}\frac{d\sigma}{dC}$$

where U = excess of substance in the surface layer
C = concentration in bulk of liquid
σ = surface tension
R = gas constant
T = absolute temperature

There will thus be a reduced concentration in the surface if the surface tension *increases* with concentration, and an increased concentration in the surface if the surface tension *decreases* with concentration. The latter is the general case; the former case is referred to as negative adsorption. For other references to work on adsorption from solutions, see Holmes.[2]

Experimental Work. Attempts to verify this equation experimentally have been made. Miss Benson compared the amyl alcohol content of the froth produced on an aqueous solution of the alcohol in water by air-bubbling, with that in the body of the solution. The concentration in

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[1] 'Adsorption of Gases by Solids : Experimental Methods.' H. S. Taylor, *Faraday Soc. Report*, 1932.
[2] *Laboratory Manual of Colloid Chemistry*. John Wiley & Sons (New York).

the froth was found to be about 5 per cent higher than that in the original solution. Lewis attempted a quantitative verification of the expression. The drop-weight méthod for determining interfacial tensions was used. The solution, one of sodium glycocholate in water, was allowed to flow into paraffin oil; the interfacial tension was measured for a number of concentrations and the σ-C curve plotted.

An emulsion of oil and solution was then made and the average size of the oil globules measured microscopically. From this the total surface oil-solution is calculated. The drop number of the emulsion was then obtained, the interfacial tension so obtained being assumed independent of the globules. The corresponding concentration is then obtained from the σ-C curve. The change in concentration of the solution due to adsorption on a known area of oil surface is then known.

The values thus obtained were found to be twenty to thirty times greater than those calculated from the Gibbs' equation.

While the term adsorption is restricted to surface effects, solution in the interior of the substance is called absorption. McBain has suggested the adoption of the term *sorption* (a term now generally used) to include the whole phenomena of the taking up of a gas by a solid.[1] Adsorption reactions are considered in the next section.

For the application of colloidal methods in biology and medicine, see latest edition of H. Bechhold, *Die Kolloide in Biologie und Medizin*.[2]

[1] See Mee, *Physical Chemistry*, Heinemann, 1934.
[2] Verlag von T. Steinkopff (Dresden).

SECTION 2 : ADSORPTION

Adsorption consists in the addition to the surface of a solid of molecules, colloidal particles or small particles of solid. The phenomenon is essentially a surface effect and is therefore particularly in evidence in the case of highly porous solids.

Adsorbents are used for a variety of technical purposes of which the following may serve as examples : the removal of colour from sugar solutions and the purification of animal, vegetable and mineral oils ; the separation of petrol from natural gas and the recovery of benzene ; the dehydration and purification of air and other gases ; the recovery of precious metals like gold and silver ; the elimination of bacteria and toxic substances from the digestive tract ; the purification of enzymes.

Much work has been done on the quantitative aspect of the subject and Freundlich (Kapillarchemie) represents by the so-called Adsorption Isotherm the relation between the mass of substance adsorbed and the concentration of this substance when equilibrium has been reached : this empirical equation is

$$\frac{x}{m} = a \cdot c^{1/n}$$

in which x = mass adsorbed

m = mass of adsorbent

c = the equilibrium concentration or pressure

and a and n are constants.

In true adsorption n is greater than 1, while in solution n is equal to 1. The value of the constant a will be proportional to the area of the active surface. The form of the experimental curves is shown in Fig. 19 (V *) where the volumes of nitrogen, carbon dioxide, and benzene adsorbed on 1 gram of charcoal are plotted against the partial pressure of the gas. It will be observed that nitrogen, the gas with the lowest boiling-point, is the least adsorbed : with the other gases, at very low partial pressures proportionately very large amounts are adsorbed and the amount adsorbed is nearly proportional to the partial pressure, i.e. $n = 1$: at rather higher partial pressures comes the region in which the Freundlich isotherm holds and finally a stage is reached when a further increase in pressure does not increase the amount adsorbed and $n = 0$.

The Freundlich equation can be written

$$\log \frac{x}{m} = \log a + \frac{1}{n} \log c \qquad .$$

hence if $\log x/m$ is plotted against $\log c$ a straight line should be obtained which cuts the ordinate axis in $\log a$ and has a slope equal to $1/n$.

Langmuir carried out experiments on the adsorption of gases on plane

surfaces of, for example, materials like glass or platinum. He concluded that the adsorbed layer was only one molecule thick; hence the necessity for a very large surface to adsorb useful amounts. It is calculated that in the case of silica gel the average pore diameter is of the order of 4×10^{-7} cm.,
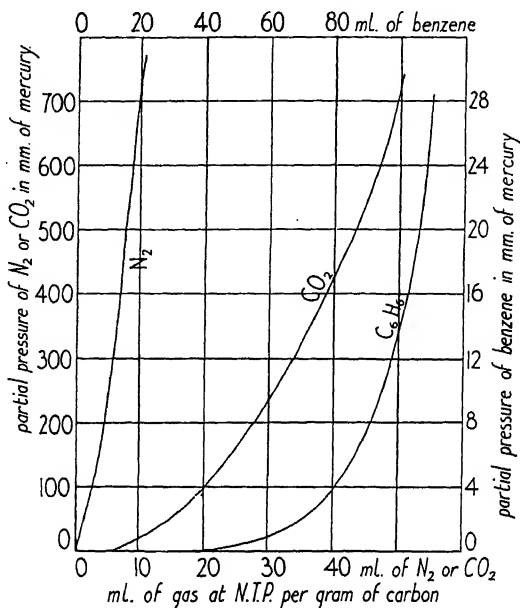
FIG. 19 (V *)

that is, about ten times the diameter of the average molecule : this gives a surface area of more than a million square centimetres to 1 ml. of the adsorbent.

Langmuir found that at low gas pressures the expression

$$x = \frac{a.b.p}{1 + a.p}$$

where a and b are constants gave better results than Freundlich's equation, but it was not applicable at higher pressures.

Determination of the Adsorption of Acetic Acid on Animal Charcoal. Six conical flasks are required and from a burette or pipette the following amounts of 1·0 N. acetic acid are added 2, 5, 10, 20, 50, and 100 ml. respectively : then a measured volume of water is added to make the total volume 200 ml. in each case : great exactness in measuring these volumes is unnecessary. Each of the six solutions is now titrated with 0·1 N. sodium hydroxide, using appropriate volumes of the solutions, e.g. 50 ml. of the first and 5 ml. of the last.

With a pipette transfer 100 ml. of each solution to a conical flask provided with a cork, and to each flask add 2 grams of animal charcoal. Shake each flask from time to time during half an hour. Allow the charcoal to settle and then pipette out the same quantities as before for titration.

The concentrations now obtained are the equilibrium concentrations, c in the equation. In each case, from the known concentrations of 100 ml. before and after the treatment with charcoal, work out the mass adsorbed x and since m is 2 grams, get x/m. Now plot the adsorption isotherm x/m, the mass of acetic acid adsorbed on unit mass of charcoal against c, the equilibrium concentration.

Next plot $\log x/m$ against $\log c$ and draw the best straight line through the points. Where this curve cuts the x/m axis, $\log k = \log \dfrac{x}{m}$ and $k = x/m$. The tangent of the inclination of the curve to the $\log c$ axis gives the constant $1/n$.

To show that the Adsorption of Acetic Acid on Charcoal is Reversible. In each of four flasks put 50 ml. of 0·1 N. acetic acid and 2 grams of animal charcoal. Shake for 15 minutes, by which time equilibrium will be sufficiently attained and all the samples of charcoal will have adsorbed the same mass of acid. To flasks 2, 3, and 4 add respectively 50, 100, and 150 ml. of water and shake for 15 minutes. Allow the charcoal to settle and from the first flask remove 25 ml., from the others 50 ml. and titrate with 0·1 N. caustic soda. Also titrate 25 ml. of the original 0·1 N. acetic acid. Now work out the mass of acid adsorbed per gram of charcoal (x/m) in each case and plot against the equilibrium concentration and show that the same curve is obtained as in the previous example.

The Mechanism of Adsorption. It must be remembered that the adsorbents used in practice have a cellular structure and there is a labyrinth of fine capillaries to be considered as well as the large surface area. In some cases there is some resemblance to chemical reaction, while in others we find inactive gases like helium or argon adsorbed by carbon, and inactive substances on platinum. If we look upon it as loose chemical combination we find that there are no stoichiometric relations apparent and, provided that excess of the adsorbent is present, decomposition is not independent of the mass remaining combined, but varies with this mass as shown by the curve. Some writers consider the effect due to the unsaturated valencies at the surfaces of the crystals while others would ascribe it to surface tension only. Having regard to the structure of the materials used it may be that both effects come into play. Thus with gases the first effect might be the formation of a layer of adsorbate on the outer surface, then diffusion through the capillaries and perhaps liquefaction there. With substances in solution diffusion through the capillaries would be a much slower process and these might even become clogged up by the large molecules present in some cases. Adsorption on the surface is probably very rapid, too rapid to be a controlling factor, which is probably the rate of diffusion through the capillaries. Hence in removing traces of colouring matter from solutions an adsorbent in the form of a very fine powder would be more rapid than granules : for technical purposes, however, there are disadvantages in the use of too fine powders.

In the case of gases at low partial pressures the rate of removal is very great : thus in a gas-mask the air is not in contact with the activated carbon for more than 0·1 second, but in this time the concentration of a toxic gas may be reduced from 100 to less than 1 part per million.

Temperature Effect. A rise of temperature decreases the amount of substance adsorbed : thus Dewar, experimenting on the adsorption of the low boiling-point gases argon, helium, hydrogen, nitrogen, oxygen, &c., by means of charcoal in order to obtain a high vacuum, found that the mass of gas adsorbed was proportional directly to the pressure and inversely to the absolute temperature (he also found that the best adsorbent charcoal was that made from coco-nut shell). In technical work, and particularly in the case of solutions, the effect of a rise of temperature in increasing the rate of diffusion more than compensates for the decrease in the adsorptive power.

Selectivity. Natural gas is a mixture containing a large number of hydrocarbons of the paraffin series. When activated carbon is first exposed to this mixture it adsorbs all the components, but those of higher boiling-point in greater proportion than those of lower boiling-point, so a partial separation of the mixture is obtained. If now this carbon is treated with more natural gas, it is found that the lighter molecules are displaced from the carbon and the heavier constituents are adsorbed in their place. By this means the gas is stripped of all its petrol, and when the carbon is treated with steam the petrol is driven off and is condensed along with the steam.

One adsorbent may be much more efficient than another for the adsorption of a particular substance (see below), thus activated carbon is three times as effective as silica gel for the adsorption of carbon tetrachloride or benzene. Activated carbon adsorbs hydrocarbon vapours in preference to water vapour while with silica gel the reverse is the case. Thus wet carbon will adsorb benzene, but wet silica gel will not do so.

In the case of the removal of dyes from solution the pH value of the solution is important : most dyes are negatively charged like methylene blue and these are best adsorbed from acid solution : positively charged dyes like ponceau red are better adsorbed from alkaline solutions. With neutral substances like sugar the pH value has no effect.

Technical Adsorbents. Many substances such as fuller's earth, acid-treated clays, bauxite, and bone charcoal are used, but the most important at the present day are activated carbon and silica gel (recently alumina gel has been used).

Activated Carbon. Organic substances are heated to a more or less high temperature in the absence of air and in some cases in the presence of certain solids, liquids or gases which act as activators. Activated carbon is thought to owe its increase in activity to the hindering of the formation on the active surface of a layer of the products of partial decomposition of the organic substance used. The activity of the resulting carbon can be varied within wide limits by variations in the organic substance used, the kind and amount of activator and the time and temperature of the process. The methods of activation may be divided into two groups : in the first gases, vapours or mixtures of these are passed over the heated material, a typical example being steam. In the second case solid or liquid chemicals or solutions are used : thus the original material may be mixed with zinc chloride, then carbonized, and finally the zinc chloride washed out.

Silica Gel is so called because it was a gel at one stage of its manufacture. The finished product is a hard glassy material composed of silica with about 5 per cent of water and similar in appearance to clear quartz sand. It is highly porous and is characterized by the uniformity in size and arrangement of the pores. It is made by treatment of a solution of sodium silicate with dilute sulphuric acid, gelatinizing the silicic acid, washing and activating. This last is a carefully controlled dehydration and on it depends the extent of the surface and the number and size of the pores. It is a specific adsorbent for water and will take up 40 per cent of its weight thereof. It is used for the adsorption of gases like carbon dioxide, sulphur dioxide, and ammonia, and for the elimination of gum in the refining of petrol, but it is not such a good clarifier or decolorizer as activated carbon. It is an ideal catalyst carrier as, for example, for platinum in the contact process for sulphuric acid. Air floated powders known as 'flowers of silica gel' are used as deodorizers in skin-dusting powders and on the human body under plaster of Paris.

Testing Technical Adsorbents. There is no universal best adsorbent : one may be the best in one case and not in another : each must therefore be tried out for the desired purpose, and if possible on the works scale. The interpretation of laboratory results requires great experience.[1]

In testing the adsorptive power for gases and vapours the adsorption isotherm must be obtained for the particular gas or vapour in question. This may be done by the static method in which one waits till equilibrium is attained and then obtains the mass adsorbed by weighing or by calculation from the original and final partial pressures. In the dynamic method a known mixture is passed over the adsorbent to saturation and the mass taken up determined.

The filter limiting value is also useful : here a gas vapour mixture in known proportions is passed over a determined mass of adsorbent at a definite rate until the first traces of vapour which have escaped adsorption can be detected in the effluent gas and the mass of vapour adsorbed up to this time determined.

Another standard test is the determination of the power of removing iodine from solution in toluene.

The heat of moistening when 1·5 grams of adsorbent is added to 10 grams of benzene is said to be proportional to the adsorptive power in many cases.

Use of Adsorbents in Gas Masks. As an example we may give the structure of the Universal gas-mask of the Bureau of Mines, U.S.A., which is capable of reducing the proportions of toxic gas from 100 to 1 part per million in 0·1 second and which has a life of 6 hours.

The air first passes through a layer of activated carbon for the removal of organic vapours, alcohol, aniline, benzene, carbon disulphide, carbon tetrachloride, &c. : next a cotton-wool filter removes suspended solids, smoke, mist, and dust ; a layer of caustic soda on pumice stone combines with acid gases and chlorine ; calcium chloride takes up water and above

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[1] F. Krczil, *Untersuchung und Bewertung technischer Adsorptionsstoffe*, Leipsig, 1931.

this a layer of a synthetic material (hopcalite) removes carbon monoxide by catalytic oxidation, and finally silica gel takes up ammonia and any vapours which have escaped removal and also prevents moisture getting back to the hopcalite.

Adsorption in Organic Chemistry.[1] Adsorption may be used for the separation and purification of a number of substances which are very difficult to separate by other means. The adsorbents used are fibrous alumina, calcium oxide, calcium hydroxide, silica gel, charcoal, and the weak adsorbents calcium carbonate, sugar, and talcum. The form of adsorption tube is shown in Fig. 20 (V *): it has a length of 3–15 cm. (sometimes 50 cm.) and a diameter from 1–3 cm. (or more). The wire gauze shown in the diagram may be replaced by sintered glass. The filling has to be carried out with care so as to avoid the formation of channels through which the liquid can run easily: the adsorbent is therefore to be added in small amounts and pressed down with a glass rod before the next addition is made or the powder may be suspended in some liquid like benzene and allowed to settle down.
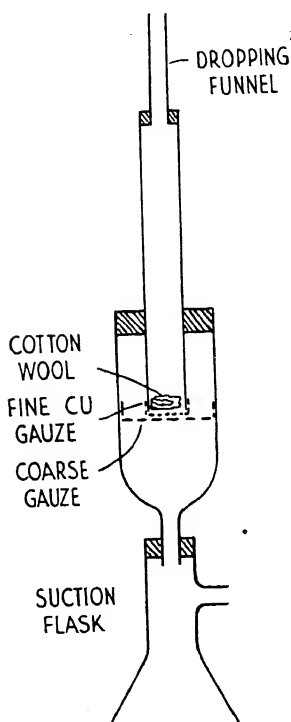
When the tube has been packed with adsorbent it is filled with petroleum ether and the vacuum started (60 mm.): when the liquid is about 2 cm. above the top of the adsorbent the tap of the funnel is opened and the solution is allowed to enter: the solution is followed by petroleum ether and then by a current of an indifferent gas to remove the liquid.

If the different fractions are coloured the separate layers are readily recognized: they are mechanically scraped off and each layer is lixiviated by warming with petroleum ether

FIG. 20 (V *)

or benzene. If the substance is not coloured the adsorbent is removed for lixiviation in small equal fractions.

Application of Adsorption Methods. The adsorption affinity of different compounds is in the order alcohols, ketones, esters, hydrocarbons; the last being the least adsorbed: it also depends on the number of hydroxyl groups and on the number of double bonds. Thus for the carotinoid alcohols the series commencing with the most adsorbed is fucozanthine ($C_{40}H_{56}O_6$), violazanthine and tarazanthine ($C_{40}H_{46}O_4$), flavozanthine ($C_{40}H_{54}O_3$), zeathanthine and luteine ($C_{40}H_{35}O_2$). The effect of double bonds (D) is shown by the hydrocarbons lycopin (13D), γ carotin (12D), β and α carotin (11D). Very small constitutional differences alter the adsorptive affinity and so make separation possible (see below). Some examples in which the method has been used are separation of lycopin,

[1] Bernhauer, *Einführung in die organische-chemische Laboratoriumstechnik.*

α, β and γ carotin in which the proportions may be very different,[1] separation of α and β carotin by calcium oxide and calcium hydroxide,[2] separation of *cis* and *trans* isomers, e.g. crocetin.[3] As a practical example of chromatographic analysis a benzene extract of fresh leaves may be prepared and passed through an adsorption tube with the adsorbents arranged as shown in Fig. 21 (V *). The calcium carbonate should be dried at 150° for 2 hours. The alumina is prepared by precipitating any aluminium salt with ammonia, coagulating, washing and drying: then grind to a fine powder and activate in a stream of carbon dioxide at 200°.

Examples of the separation of colourless substances are vitamin A with calcium hydroxide,[4] separation of hydrocarbon and alcohol, with alumina, the alcohol being adsorbed and the hydrocarbon being in the filtrate, e.g. oleanol and oleanylan or geraniol and limonene.[5]

A further very important use of adsorption is in the purification of enzymes, &c., and other indefinite plant and animal substances. The raw material is treated with a suitable solvent and the solution is clarified and subjected to a preliminary purification. The adsorbent is then added and when equilibrium has been reached is separated and lixiviated.

The chief adsorbents used are inorganic hydroxides, carbonates, and salts, e.g. argillaceous earth, iron hydroxide, zinc hydroxide, stannic acid, silicic acid, calcium and lead phosphate, barium sulphate, asbestos, kaolin, talc, and so on. Organic substances such as tristearin, cholesterol, casein, fibrin, wool, and silk have been used, and of special importance is the use of well-defined colloidal aluminium hydroxide gels.
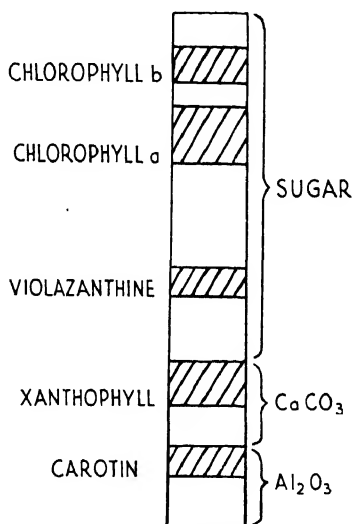
FIG. 21 (V *)

The procedure consists first in freeing the enzyme by rupture or destruction of the cell walls by such methods as vacuum drying or treating with dehydrators like alcohol or acetone, triturating with quartz sand and pressing out the juice, destroying the cell-wall by plasmolysis or freezing. The liquid so obtained is digested with acids, alkalis or salt solutions or glycerine and submitted to a preliminary purification by such methods as treating with kieselguhr and centrifuging, precipitating the enzyme with acetone, alcohol, &c., removal of salts by dialysis. Alcohol or acetone is usually added and then the adsorbent is stirred in the liquid for 10 minutes or more. The adsorbent is separated by centrifuging: the final process

[1] Winterstein and Ehrenberg, 1932, H, *207*, 25; Kuhn and Brockmann, *Ber.*, 1933, *66*, 407.

[2] Karrer and Walker, *Helv. chim. Acta.*, 1933, *16*, 641.

[3] Kuhn and Winterstein, *Ber.*, 1931, *64*, 326; 1933, *66*, 209.

[4] Karrer and co-workers, *Helv. chim. Acta*, 1933, *16*, 625.

[5] Winterstein and Stein, 1933, H, *220*, 247, 263.

consists in lixiviation by digestion and stirring for a long time : water is often used for this purpose and a change of reaction is often necessary using weak alkalis like ammonia, sodium bicarbonate, disodium phosphate, or acids like acetic.

The adsorption method has also been used in the isolation of water-soluble vitamins.

Adsorption Indicators. Since 1927 the use of adsorption indicators in volumetric precipitation methods has been developed largely by the work of Fajans and of Kolthoff and their co-workers. Very dilute solutions may often be titrated by this method with accuracy. As an example of their use we may cite the titration of 25 ml. of a neutral 0·05 N. solution of a chloride with silver nitrate solution using as indicator not more than 2 drops of 0·2 per cent alcoholic solution of fluorescein (the amount of indicator recommended is 1×10^{-3} mols. to 1 mol. of the precipitate : the titration should be carried out rapidly.

During the course of the titration the solution retains the greenish-yellow colour and the fluorescent appearance due to the indicator until exactly the equivalent amount of the silver ion has been added : on the
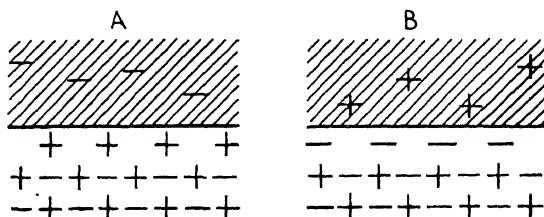
FIG. 22 (V *)

addition of one drop more of silver nitrate the precipitate and also the colloidal suspension of silver chloride take on a distinct reddish tint.

The change is reversible since the addition of more chloride causes the reappearance of the fluorescence and the greenish-yellow colour of the fluorescein.

A theoretical basis for the mechanism of the action has been worked out by Fajans.[1] Lottermoser[2] showed that when potassium chloride is precipitated with silver nitrate, the precipitate of silver chloride is negatively charged with respect to the solution in the presence of excess of chloride ions, while if there is an excess of the positive silver ions the precipitate of silver chloride becomes positively charged. This is assumed to be in the first case due to the adsorption of chloride ion so that the state of the precipitate may be represented by [AgCl]Cl⁻ : in the second case the state of the precipitate is shown by [AgCl]Ag⁺.

Fajans represents diagrammatically as shown in Fig. 22 (V *) the condition of an adsorbent in contact with its saturated solution either in pure water or in the presence of positive or negative ions. In A the two lower lines represent the ion lattice structure of, for example, silver chloride;

[1] *Chem. Anal.*, 1935, *33*, 161, 207.
[2] *J. prakt. Chem.*, 1905, *72*, 39 ; 1906, *73*, 374.

the third line shows the adsorbed ions, in this case Ag^+: the charged body $[AgCl]Ag^+$ will then attract the negative ions in the solution with their 'water envelopes'. In B we have the conditions for a negatively charged body such as $[AgCl]Cl^-$.

Taking as an example the titration of potassium bromide with silver nitrate in the presence of eosin as indicator: in the early stages while there is excess of bromide, the complex will have the structure $[AgBr]Br^-$; this will repel the coloured negative ion of the eosin and the solution will show the greenish yellow fluorescence of eosin, while the precipitate of silver bromide will have its ordinary pale yellow colour: these conditions will continue till the equivalent amount of silver ion has been added. With the addition of the first drop of excess of silver nitrate the complex becomes $[AgBr] Ag^+$ and this adsorbs the negatively charged eosin anions while repelling the remaining free silver ions. The adsorbed eosin shows a reddish colour due to the deformation of the electron system of the anion and at the same time the fluorescence disappears. Addition of excess of bromide ion restores the original conditions because the adsorbed eosin anions are now displaced by the negative bromide ion. The adsorbability of analogous ions increases with decreasing solubility of the precipitates formed: for example, silver iodide is less soluble than silver chloride and iodide ion is more readily adsorbed than chloride ion. Similarly, silver erythrosinate is less soluble than silver eosinate and so erythrosin is more strongly adsorbed on potassium iodide than is eosin.

In general we may say that with an acidic indicator like fluorescein it is necessary

(1) that the anion of the salt titrated should form a sparingly soluble salt with the heavy metal cation of the precipitant,

(2) part of the precipitated salt should remain in the soluble form,

(3) the precipitated salt should be less soluble than the salt of the indicator anion and the precipitating cation,

(4) this salt should be sparingly soluble and of a different colour from the original dye-stuff.

With basic indicators such as rhodanine 6G it is naturally the cation of the dye which is concerned: in some cases the colour change is not reversible.

EXAMPLES OF SOME OF THE CHIEF ADSORPTION INDICATORS WITH THEIR USES

Alizarin . .	nitrates with titanous chloride in HCl solution.
Alizarin S . .	ferrocyanides in neutral solution with lead nitrate.
Bromophenol blue	chloride and iodide with silver nitrate, bromide with mercurous nitrate.
Dibromofluorescein .	sodium hydroxide with lead acetate, bromide or iodide in weak acid solution with lead acetate, orthophosphate in neutral or weakly acid solution with lead acetate.
Dichlorofluorescein	chloride in weakly acid and very dilute solution with silver nitrate, sodium hydroxide with lead acetate, borates with lead acetate.
Diphenyl carbazide .	cyanides with silver nitrate.

Fluorescein	.	neutral halides and thiocyanate with silver nitrate,
		neutral oxalates with lead acetate,
		sodium hydroxide with lead acetate,
		some neutral sulphates with barium hydroxide.
Phenosafranine		bromide with silver,
		silver with bromide.
Tartrazine	.	silver with halides or thiocyanates.
Eosin	. .	bromide, iodide or thiocyanate in weakly acid solution by silver.
Erythrosin	.	iodide (only in the presence of twentyfold excess of manganous sulphate) by silver.

Electrodialysis of Soil Cations. The colloids present in a soil adsorb cations, and methods have been proposed for dealing with the interchangeability of these cations : such methods are Way's salt extraction method and the use of dilute acids. More recently electrodialysis has been used for the same purpose and the kind of apparatus used is illustrated by that described by Löddesöl.[1]

The apparatus consists of three glass chambers connected by wide flanges which support the membranes. The flat globular middle chamber has a wide neck at the top to allow for changes in the water due to electro-endosmose, and a glass tap at the bottom for the removal of the soil suspension : the chamber has a volume of 450 ml.

The end chambers have a capacity of 125 ml., a neck at the top for the admission of water and a stopcock at the bottom for the removal of the solutions. At the end is an aperture for the insertion of the electrodes, which are flat discs of platinum-rhodium with a diameter of 4 cm. and are brought up close to the membranes.

As membranes, parchment is recommended at the cathode and cellophane at the anode. With this arrangement the flow of water from the anode chamber to the middle compartment is found to be less than when parchment is used as anode membrane. The effective area of the membrane is 30 sq. cm. It is necessary to cool the middle chamber and this is done by means of a metal ring surrounding its neck; the ring is hollow and has a number of holes in it so that cooling water runs out and envelops the bulb in a layer of running cold water which is collected in a pan below. The change of temperature in the end compartments is controlled by a slow continuous change of the water therein, the outflowing solutions being reserved for analysis.

[1] *J. Amer. Soc. Agronomy.*

CHAPTER VI *

OPTICAL MEASUREMENTS

SECTION 1: POLARIMETRY

GENERAL **Considerations—Light Rays.** Originally Fresnel considered that the ether particles in the wave front of a light wave were in motion in all directions which were perpendicular to the direction of propagation of the light, but that under certain circumstances the vibrations became constrained so that they were all parallel to one another: the light was then said to be plane-polarized. On the electro-magnetic theory of light it is considered that there is a magnetic disturbance in the plane of polarization and an electrical disturbance at right angles thereto. For the purposes of explanation it is simpler to consider only one kind of vibration, e.g. electrical ones, which in polarized light are all in one plane.

If a ray of ordinary (unpolarized) light is passed through a crystal of Iceland spar along the direction of the crystallographic axis of the crystal, nothing noteworthy is observed; but if it is passed in any other direction it is found to be split up into two rays, each of which is plane-polarized in a plane perpendicular to that of the other. Each of these rays can be split up again into two by passage through a second crystal, and so on. When the refractive index of the crystal is measured for the two rays it is found that a constant value of 1·658 for μ_D is obtained for one ray (termed the ordinary ray), but that the value of the other ray varies between 1·486 and 1·658, depending upon the direction through the crystal along which the ray passes. This is called the extraordinary ray. The possibility of further splitting up of the beams is not of immediate practical interest and will not be considered here.

The Nicol Prism. The two rays can be separated by means of the Nicol prism. Originally this is made by slicing a rhomb of Iceland spar diagonally and symmetrically through its blunt corners, polishing the cut faces and cementing them together again with Canada balsam. The index of refraction of Canada balsam is 1·55, which is less than that of the crystal for the ordinary ray, and intermediate between the maximum and minimum values for the extraordinary. The critical angle for the ordinary ray is therefore 68°, while that for the extraordinary ray is greater than 68°, except when this has its maximum refractive index, that is, when it is travelling along the optic axis. Fig. 1 (VI *) shows the plane of section cutting the natural crystal, and Fig. 2 (VI *) shows a section through the plane ABCD. AO gives the line of the optic axis. It will be seen that the extraordinary ray formed from a horizontal ray enter-

ing the crystal is inclined at about 75° to the optic axis and therefore has a low refractive index. As shown in the figure, since the horizontal ray does not strike the surface AD normally, it is refracted and split up into the two rays—QR, the extraordinary; and QX′, the ordinary. The latter strikes the surface AC at an angle of about 72°, and because this is greater than the critical angle for the ordinary ray it is reflected along X′T and passes out at the side of the prism. The former strikes the surface AC at a smaller angle and, in addition, the critical angle of this ray is larger and is not exceeded. The ray there- fore passes along PQRS, emerging parallel to its original direction but dis- placed laterally.
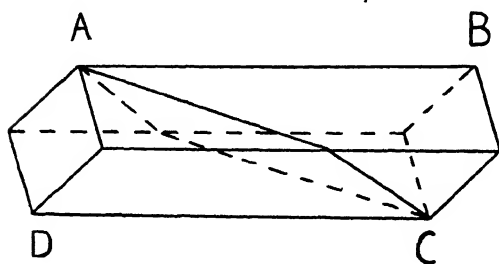
FIG. 1 (VI *)

The Nicol prism has been modified by Lippich, so as to have square ends and to have a film of linseed oil instead of Canada balsam. The prism is cut out of the block so that the optic axis is in the plane of the end.

The square-ended form is generally used at the present time, as is also linseed oil. In the Glan form the optic axis is parallel to the plane of section, while in the form technically called the Lippich Nicol, the optic axis is at right angles to the plane of section. The square end reduces loss of light by reflection and the displacement of the image on rotation of the prism. The displacements in the emergent ray may be taken to be parallel to AD in Fig. 2 (VI *). If the ray traverses a second
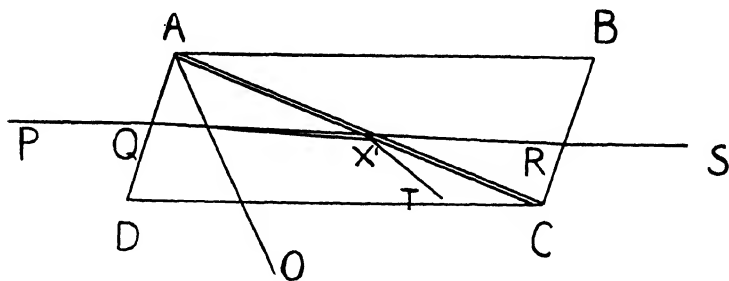
FIG. 2 (VI *)

nicol placed similarly to the first, i.e. so that A′D′ is parallel to AD, the polarized ray is able to pass through. If A′D′ is perpendicular to AD the polarized ray is reflected out of the side of the second nicol and no light passes out through the end; while if A′D′ and AD are inclined at an angle between 0° and 90° the plane-polarized ray is split up into two rays by the second nicol and only one of these is able to pass out at the end. Therefore, as the second nicol is rotated through 180° in either direction, the light decreases from a maximum to zero and then increases

to a maximum again. When the nicols are placed so that no light passes through them (nicols so placed are said to be *crossed*), it is found that if certain substances are placed between the two nicols a certain amount of light is able to pass through. Substances which have this property are said to be 'optically active' and to 'rotate the plane of polarization'. If the second nicol is turned through a small angle complete darkness can be obtained again. This small angle may be to the right or to the left, and the rotation is said to be dextro- or laevo-rotation respectively. If a rotation to the right of 15° produces darkness, a rotation to the left of 165° will produce the same result, but in taking the sign of the rotation the smaller of the two angles is always understood. Examples of optically active substances are quartz, oil of turpentine, and solutions of cane-sugar.

The amount of rotation produced depends upon the nature of the substance and its thickness, the wave-length of the light, the temperature and, in the case of solutions, on the concentration and the nature of the solvent.

Expression of Results. In recording the results of measurements the following terms are used:

The 'observed rotation' in the case of a pure substance is the angle through which the plane of polarization is rotated by a layer of the substance 1 decimetre in thickness, e.g. $\alpha_D^{30°} = + 31.42°$ means that at 30° C. for sodium light, a layer of the substance 1 decimetre thick rotates the plane of polarization 31.42° in a clockwise direction.

The 'specific rotation' is denoted by $[\alpha]$, thus $[\alpha]_D^{t°} = \dfrac{\alpha_D^{t°}}{d}$, when d is the density of the substance at $t°$.

In the case of a solution the 'specific rotation' $[\alpha]_D^{t°C.} = \dfrac{\alpha_D^{t°} \times 100}{p \times d}$ where p is the percentage composition by weight.

The 'molecular rotation', $[M]_D^{t} = [\alpha]_D^{t°} \times M$, where M is the molecular weight.

For accurate work the sodium flame is sometimes replaced by a mercury arc and the rotations noted with the two prominent lines in the mercury arc, e.g. the Hg green and the Hg yellow light and the results expressed as follows, taking a particular example:

Rotation of d-phenylbenzylmethylallylammonium d-α-bromo-camphor-sulphonic acid.[1]

An aqueous solution was made containing 0.1655 gram in 30 ml. at 14° in a 4-decimeter tube. It gave:

	Hg green	Hg yellow	Na Yellow
α	+ 2.23	+ 1.91	+ 1.80
$[\alpha]$	101.1	86.5	81.5
$[M]$	554	474	447

The rotation dispersion for $Hg_{green}/Na_{yellow} = 1.239$ and for $Hg_{yellow}/Na_{yellow} = 1.061$. Taking the molecular rotation of the d-bromo-camphor-sulphonic acid ion as $[M]_D = 279$, this gives the molecular rotatory power of the d-phenylbenzylmethylammonium ion $[M]_D = 168$.

[1] Reilly, *Trans. Chem. Soc.*, 1917, *111*, 24.

Polaroid. In 1932 a patent was taken out by E. H. Land [1] in which he utilizes the dichroic properties of certain substances to filter out of common light a component with high percentage plane polarization, by transmission through any sized aperture desired. He utilizes a thin film of nitrocellulose packed with ultra-microscopic crystals of herapathite with their optic axes all parallel to one another. This film behaves like a single extended crystal, but since the crystalline particles overlap in the direction of the thickness of the film the transmitted beam is absorbed more than is a single crystal and the film has a smoky brown appearance.

Herapathite [2] was discovered by Dr. W. B. Herapath in 1851,[3] and it is a double salt of quinine sulphate and quinine iodo sulphate. If the quinine molecule is represented by X, it is stated to have the formula $4X.3H_2SO_4$, $2HI$, $6H_2O$. A similar type of compound with strychnine was discovered by Herapath later. The double refracting crystals are minute hexagonal plates and a 0·005-inch thick plate will completely absorb one of the rays and the other ray is transmitted with only slight absorption. If mounted in Canada balsam dissolved in xylol, the iodine disappears and the crystals lose their polarizing properties. In ether, it is more permanent. This polarizing material is known under the name 'Polaroid'. It generally consists of the film prepared as described above between two glass plates. For other uses for this material, see *Engineering*,[4] e.g. in photography, and in detection and analysis of strains in transparent material. As stated, this film of the 'Polaroid' disc consists of a fixed suspension of dichroic crystals which are in substantially uniform orientation in the cellulose matrix. The film is usually between 0·001 and 0·004 inch in thickness; the degree of polarization of the transmitted light increases with the thickness. When light enters one of the crystals it is divided into two components polarized at right angles to each other. One of the components is absorbed to a greater extent than the other owing to the dichroism of the crystals. The transmitted light may be considered as being partially plane polarized in the usual sense as if it were a mixture of plane polarized and unpolarized light. For further details of 'Polaroid' the paper by Grabau [5] may be consulted. The polarizing property of 'Polaroid' was found by Ingersoll et al.[6] to be limited almost entirely to the visible spectrum and to fall off very rapidly in the infra-red and violet regions. While it cannot replace the nicol in measuring instruments in which polarization must be complete it can be used [7] with great advantage in photo-elastic apparatus, strain recorders and projecting lanterns, microscopes, telescopes, ophthalmic instruments in which the nicol restricts the aperture or interferes with the definition of the optical image.[8,9]

[1] B.P. 412,179—1932. See also U.S. Patents 1,918,848, 1,989,371, 1,951,664, 1,956,867, 2,011,553.

[2] See *Nature*, 1936, *138*, 312, for a good account of polaroid and a discussion on light polarization generally and its technical application.

[3] *Phil. Mag.*, 1851, *3*, 161.   [4] 1936, *142*, 235.   [5] *J. Opt. Soc. Amer.*, 1937, *27*, 420.

[6] *Ibid.*, 1936, *26*, 233.   [7] *Nature*, l.c.

[8] A full discussion with bibliography is given by Freundlich in *Photographic J.*, 1936, *76*, 395.

[9] See also Freundlich, 'Polaroid Films', *Chemistry and Industry*, 1937, 698, and Grabau, 'Polarized Light enters the World of Everyday Life', *J. Appl. Phys.*, 1938, *9*, 215.

Laurent Polarimeter. In carrying out measurements, it is extremely difficult to judge when the minimum amount of light is passing through, so that in practice a different method is used. In the Laurent polarimeter use is made of a quartz half-wave plate.

Let Fig. 3 (VI *) represent a plate of quartz in which the optic axis is parallel to OY. Let this plate be placed so that the direction of vibration of the polarized light which falls upon it·is along OA. This wave may be regarded as being resolved into two components, the ordinary ray along Ox and the extraordinary ray along Oy. If at the moment the wave enters the plate we consider the ether particle at A, its displacement may be along OA, and the two components of this displacement will be along Ay and Ax. The ordinary and extraordinary rays travel at different rates, so that after a short time the extraordinary ray will be half a wave-length behind the ordinary. Therefore, when one component is along Ax the other will be along yA, and the resultant will be along yx; the plane of polarization has thus been turned through an angle $2r$ where r is the angle AOY. The thickness of the half-wave plate will depend upon the wave-length of the light used, so that monochromatic light is necessary. When such a half-wave plate is placed between the polarizer and the analyser, so as to cover half of the field of the former, the two halves of the field will in general appear of different brightness when viewed through the analyser. When the latter is placed so as to give complete extinction of the light which does not traverse the quartz plate, the part of the field due to the light coming through the quartz plate will appear bright. If
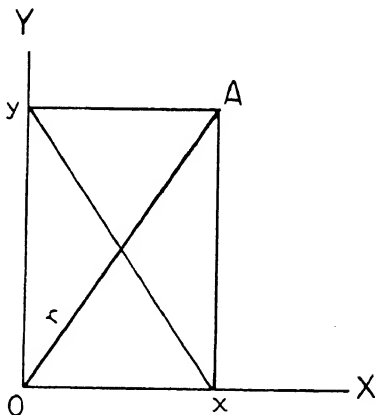
FIG. 3 (VI *)

the analyser is turned through an angle $2r$, the appearances of the two halves of the field will be reversed; while if it is turned through an angle of r the two halves of the field will be of equal intensity, both being equally dark. If the analyser is now turned through 90° the two halves will appear equally bright, and it is this condition which is judged most readily by the eye. The quartz plate is usually in the form of a semi-circular disc, a vertical strip or a small central disc, and is fixed in position. The angle r is varied by rotating the analyser, which is movable over an angle of about 15°, its position being indicated by a pointer moving over a scale. In practice an angle of 2°–3°, corresponding to a half-shadow angle of 4°–6°, is usually found suitable. If the angle is made less the reversal of the two fields is caused by a small movement of the analyser; too small an angle makes it difficult to judge the relative intensities with accuracy. The general arrangement of the optical parts in the Laurent polarimeter is shown in Fig. 4 (VI *), where a represents the polarizer, b the half-wave plate, c the analyser, and d and e the telescope lenses. In the Lippich polarimeter the place of the quartz half-wave plate is taken by

a second small Nicol prism which produces a similar result, but has the advantage that it can be used with monochromatic light of any wavelength, whereas the half-wave plate can be used only for the light of that particular wave-length for which it has been designed. In some instruments two additional nicols are used, as shown in Fig. 5 (VI *), thus giving

e d c   b   a

FIG. 4 (VI *)

a triple field. The two nicols are inclined at a small angle to one another, and the telescope is focused on the edges D and E.

Fig. 6 (VI *) shows the complete instrument in section. Light from the aperture on the right is collimated by the lens S and thus passes through the polarizing nicol P and the auxiliary nicols NN. The nicol P is attached
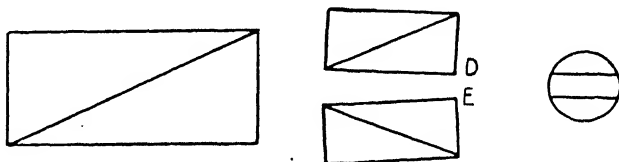
FIG. 5 (VI *)

to the arm Q, which moves over the graduated arc R. This enables P to be rotated through any desired angle in order to alter the half-shadow angle : the relative positions of Q and R are fixed by the screw shown. After passing out of the plate-glass window M, the light traverses the tube LK, which contains the solution under examination. The system
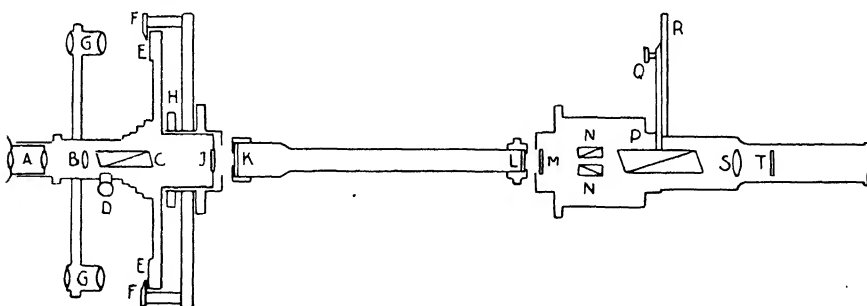
FIG. 6 (VI *)

containing JCBA is all rotatable about the horizontal axis, while the framework carrying the verniers FF is fixed in position. EE is a disc attached to the rotatable system and has a scale of degrees and fifths of a degree; this scale moves under the verniers FF, which are marked to read 0·01°. J is a plate-glass window, C the analyser nicol, and AB the telescope. GG are small microscopes for reading the verniers. When the half-shadow angle is altered by moving Q the zero of the instrument is changed. An

adjusting screw at D enables the zero to be adjusted by a rotation of the nicol C.

Light Sources. As a source of sodium light the United States Bureau of Standards found that a stick of fused sodium carbonate in the oxy-hydrogen flame gives an intense yellow light; it requires an assistant to attend to it. A piece of pumice stone soaked in sodium chloride solution, dried and heated in a Bunsen flame, gives fairly good results. The light from the flame is passed through a tube 10 cm. long containing 9 per cent potassium bichromate in water to act as a filter. Electric sodium lights have recently been developed and give a light of an intensity about twenty-five times that of an ordinary gas sodium lamp. They are enclosed in a glass bulb and fit into a socket in the ordinary way : when used on the 110- or 220-volt mains a rheostat is necessary. The spectrum consists of the two very intense D lines and a few faint lines in the neighbourhood. Because of the great intensity of the light it is possible to adjust the polarimeter for a smaller half-shadow angle so that greater sensitivity and reading accuracy is securable.

Messrs. Phillips make such a lamp consisting of a glass mantle containing a small glass tube in the ends of which two electrodes are sealed. This is the actual source of light. The tube contains a small quantity of sodium which when an electric discharge takes place in the tube, evaporating partly, gives a strong yellow light of 8 c.p. The space between the small tube and the glass mantle has been evacuated to limit the heat losses and to obtain a constant light intensity. The lamp is fixed on a hemispherical base of ' Philite ' and is covered by a mantle of the same material with a slit opening. On the base is a metal bar so that the lamp can be fixed to a stand if desired. A connexion box contains a choke coil and a condenser. For voltages other than 220–240 an auto transformer tapped at seven points between 110 and 210 volts is supplied. A tubular resistance is required when the apparatus is used on D.C. The green line of mercury vapour ($\lambda = 5{,}461$ Å) is now largely used as a standard in accurate polarimetric work. Quartz mercury lamps are obtainable which are cheap and reliable in action. The Nutting glass mercury lamp is very simple and effective ; the use of glass instead of quartz cuts out the ultra-violet light. Some form of dispersion system is necessary to separate the desired line for very accurate work, but for most purposes coloured glass filters are obtainable.

Where a number of lines are required Lowry suggests the following :

Lithium (red)	$\lambda = 6{,}708$Å
Cadmium (red)	6,438
Sodium (yellow)	5,893
Mercury (green)	5,461
Cadmium (green)	5,086
Cadmium (blue)	4,800
Mercury (violet)	4,359

The lithium line is obtained from the flame spectrum and the cadmium lines from a rotating arc, in which the electrodes rotate in opposite directions at a speed sufficient to prevent flickering. The electrodes contain 28 per cent of cadmium and 72 per cent of silver.

Temperature Control. With polarimeters which are in constant use for carrying out the same determination, satisfactory results are obtained

by enclosing the whole of the instrument in a constant-temperature chamber provided with a brine coil for cooling the air, an electrical heating coil controlled by a thermo-regulator, and a fan. For ordinary work the tube containing the solution is placed in a thermostat with glass windows and situated between the two parts of the polarimeter : with many polarimeters there is not room for a thermostat, and in such cases jacketed tubes through which a supply of water at constant temperature flows must be used instead. A device for securing the water flow is described by Lowry.

Polarimeter Tubes. Fig. 7 (VI *), *a, b, c* and *d*, shows different types of polarimeter tubes. The essential features are a tube of sufficient width to take the whole of the incoming light, parallel ends free from strain, accurate length and accurate centring of the axis of the tube. Fig. 7 (VI *) *a* shows the simplest form of tube, in which the bore is the same throughout. On the end is fixed with cement a threaded piece of metal in which
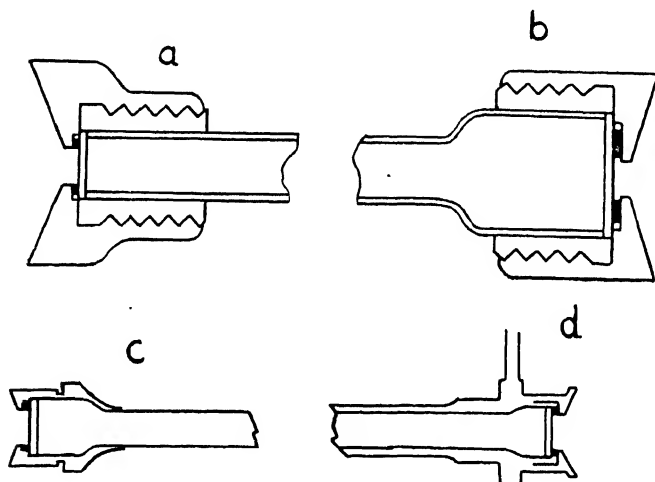
FIG. 7 (VI *)

the cap screws down. A plane glass disc is placed over the end, next a rubber ring, and then the cap is screwed down to make a tight joint. The defect of this form is the difficulty of filling so as to exclude all traces of air and to prevent the formation of air bubbles on cooling and contraction of the liquid. This defect is overcome in the end shown (Fig. 7 (VI *) *b*) where the bore is expanded near the cap so that an air bubble can be run up to this part of the tube and so got out of the field of view. The improvement in the Bates' tube shown at 7 (VI *) *c* consists in the provision of a metal collar on which the weight of the tube is supported. This prevents strain in the end glasses and accidental tightening of the caps owing to turning the tube. The Pellet tube shown at 7 (VI *) *d* has a metal jacket through which water can be circulated. Some of these jacketed tubes have an opening at the centre for the insertion of a thermometer.

Operation. The setting of the half-shadow angle is interfered with as rarely as possible. With a small angle the accuracy of the setting is increased, provided that sufficient light gets through, so that for coloured

or cloudy solutions a larger angle has to be used. For ordinary use an angle of 4° on the scale will be found satisfactory. A tube containing the solvent alone is placed in the trough, the source of light adjusted and the accuracy of the zero tested (Fig. 6 (VI *)). The disc E is turned to the zero reading, and on looking through the eyepiece a uniformly coloured field will be seen. The eyepiece is next focused on the near edges of the prisms NN, when the field will be divided into three strips ; the circle is turned slightly clockwise so that the equality of illumination of the three strips is destroyed. It is then turned slowly back by means of the fine adjustment screw below H (not shown in the drawing) until uniformity is again produced : the reading of the two verniers is recorded. The circle is now turned slightly counter-clockwise and then equality is approached from the opposite side. The mean of several pairs of readings taken in this way gives the zero. Should the zero be found to be incorrect, a slight adjustment is made by means of the screw D and the zero is redetermined, the process being repeated until a satisfactory result is obtained. The tube containing the solvent is now replaced by that containing the solution under examination. In filling the tube care has to be taken not to include air bubbles and not to screw up the caps so tightly as to strain the glass and make it doubly refracting. Now with the circle set at zero the field will be found to be non-uniform, but uniformity will be again secured by turning the circle through a small angle either to the right or to the left. The exact position of this point is found in a similar manner to that used in the case of the zero, approaching equality from both sides. The difference between the two readings gives the angle of rotation.

Adjustment of the Polarimeter. After seeing that the circle runs smoothly and that the verniers are mounted correctly they may be tested as follows :

Test the circle for eccentricity by taking the readings with left and right verniers at 0, 45, 90, 135, 180, 225, 270, 315, e.g. :

R	L	L–R
0·385	180·400	180·015
45·120	225·140	180·020
90·105	270·150	180·045
135·085	315·145	180·060
180·125	0·190	180·065
225·100	45·160	180·060
270·165	90·195	180·030
315·125	135·140	180·015

Test for inequality of division of the circle by measuring the length of the vernier at different points, e.g. :

Position of vernier zero	Error in length of vernier
360	0
40	− 0·01
80	0
120	0
160	− 0·005
200	+ 0·005
240	0
280	0
320	0

The source of light is placed in line with the axis of the instrument and in such a position as to form an image on the window of the analyser diaphragm.

The eyepiece A (Fig. 6 (VI *)) is then moved until the near edges of the Lippich prisms N are sharply in focus. The circle E is set in the zero position and clamped by means of the vertical screw below, so as to bring the slow motion into operation, and by means of this the exact setting to the zero is made. The three parts of the field should then be of exactly equal intensity. If this is not so the position of the analysing nicol C must be altered by means of the thumb-screw at D until exact equality is obtained. This setting of the zero has to be made each time the value of the half-shadow angle is altered (by means of the arm Q) ; a small half-shadow angle is used with clear transparent solutions, while a larger angle has to be used with solutions which are coloured or turbid. During a set of readings the value of the half-shadow angle is of course not to be altered. A tube having been placed in the trough, the latter is adjusted so as to get the axis of the tube in coincidence with the optical axis of the apparatus. The tube containing the solution to be examined having been put in the trough, it will be found that the equality of the field is destroyed. The circle E is unclamped and rotated until the equality is restored, the rotation being made in the direction which requires the smaller angle for this purpose. The circle is again clamped and the final adjustment for equality made by the slow motion. The mean of ten readings is taken, equality being approached alternately from each side. Since the vernier reads to 0·01° the use of the slow motion is necessary when settings are to be made to this degree of accuracy. The position of the zero is finally checked. The temperature of the solution is noted, but with the polarimeter no temperature correction for the instrument, such as is necessary with saccharimeters, is required.

SECTION 2: SACCHARIMETRY

Saccharimeters. Raw sugar solutions are far from transparent, and it is difficult, with most sources of monochromatic light at our disposal, to get sufficient light through the polarimeters already described (see later). The quartz wedge saccharimeter was devised to overcome this difficulty and to enable white light to be used. This is possible because the rotary dispersion of quartz is approximately the same as that of a sugar solution. The instrument cannot be used for solutions other than those of sugar. Fig. 8 (VI *) A shows the polarizing system usually adopted in modern instruments. The lens a converges white light on to the aperture in b; the lens c brings the light to a focus at a point (the objective of the telescope);
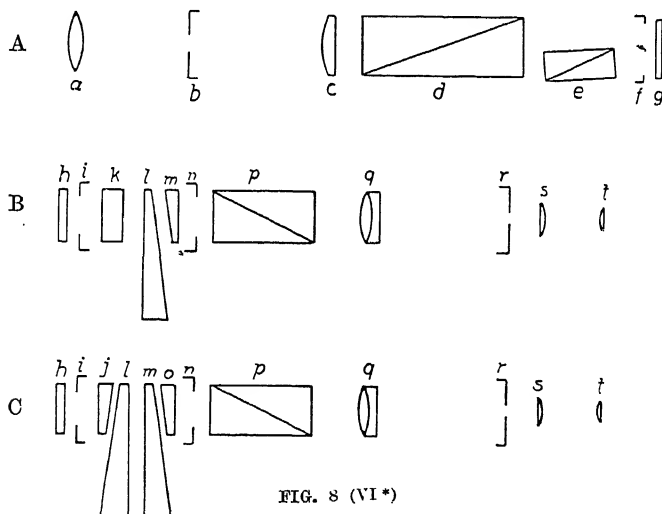
FIG. 8 (VI *)

d is the polarizing nicol and e the Lippich half-shadow nicol; f is a diaphragm and g a plane glass plate to protect the optical parts. Fig. 8 (VI *) B shows the single wedge analyser. Here k is a dextro-rotating quartz plate and l and m are laevo-rotating quartz wedges, of which m is fixed and l is movable (upwards in the diagram). The wedges are of such a thickness that when l is moved up one-fifth of its length from the position shown in the figure the sum of the thicknesses of the two left rotating wedges is just equal to that of the right rotating plate k. Light passing through the system when it is in this position has its plane of polarization unaffected; if l is moved upwards the plane of polarization will be rotated to the left, while if moved down it will be rotated to the right. If the nicols are arranged so as to give equality of the field in the absence of the quartz

plate and wedges and these are then inserted and adjusted to the zero position, the equality of the field will be undisturbed. If now a solution of sugar be placed between the polarizer and the analyser the plane of polarization will be turned to the right and the equality of the two parts of the field will be destroyed. The quartz wedge l is then moved up until the equality is once more restored, when the laevo-rotation of the quartz just balances the dextro-rotation of the sugar. The linear distance through which the wedge l is moved is proportional to the rotation of the quartz system and therefore to that of the sugar solution.

The remaining parts of the analyser are the protective plane glass plate h, the diaphragms i and n for cutting out extraneous light, the analyser nicol p, the achromatic telescope objective q, the diaphragm r situated in the focal plane of the eyepiece of the telescope in order to cut out the halo round the image, and the lenses s and t, forming the eyepiece of the telescope. The scale is graduated to read 115° dextro- and 30° laevo-rotating. In the double-wedge system shown in Fig. 8 (VI *) C, j and l are dextro-rotating wedges and m and o laevo-rotating ; j and o are fixed and m and l are both movable. If the wedge m is moved upwards in the diagram (laterally in the instrument) a laevo-rotation is produced which will compensate a dextro-rotating solution, while the wedge l can be used to compensate a laevo-rotating solution. The wedge is moved along well-fitting guides by means of a rack and pinion and the scale is fixed to the carriage ; the vernier is secured to the fixed wedge. The arrangements for observing the scale and vernier are shown in Fig. 9 (VI *), where a beam of light from the white source falls on the grey glass
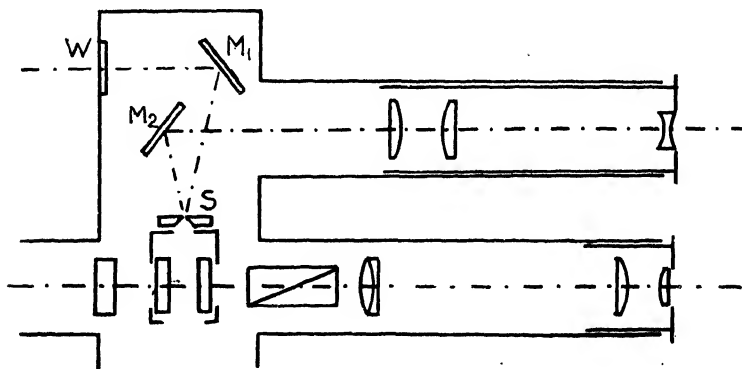
FIG. 9 (VI *)

window W and is reflected by the mirror M_1 on to the scales S and then by the mirror M_2 into a second telescope fixed above the observation telescope of the instrument. When the double wedge is used there are two scales and verniers, and in some instruments these are viewed through a single telescope, while in others two are provided.

The light is filtered through potassium bichromate solution of such a concentration that the product of the percentage concentration into the length of the column in centimetres is equal to 9. Messrs. Hilger make an aniline dye filter which gives the same results and is more per-

manent. The scales on the wedges are arbitrary and two scales are in use, namely, the Ventzke and the French scale. Each scale has a hundred divisions, but the divisions have different values on the two scales. A normal solution of cane-sugar is one which is of such a concentration that it produces a rotation of 100° on the scale when the polarization is carried out at 20°.

The International Commission for Sugar Analysis gave the following definition for the Ventzke scale : ' One dissolves 26·00 grams of pure cane-sugar in a 100-ml. flask, weighing to be made in air with brass weights, and " polarizes " the solution in a room the temperature of which is 20°. Under these conditions the instrument must read exactly 100. The temperature of all sugar solutions to be tested is always to be kept at 20° while they are being prepared and while they are being polarized.' The definition refers to the case when a 200-mm. tube is used and the 100° refers to the difference in the scale readings before and after the sugar solution is introduced. The French scale has a normal solution containing 16·29 grams of sugar in 100 ml. polarized at 20°.
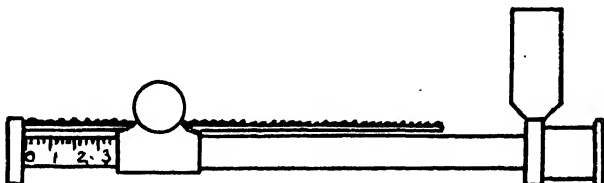
FIG. 10 (VI *)

For the verification of the scales accurately ground quartz test plates are made which give the same rotation as the normal solutions, and these are very convenient for checking the 100° point on the scale. Other points can be checked conveniently and the scale calibrated by means of the Landolt control tube shown in Fig. 10 (VI *). The length of the tube can be varied between 220 mm. and 420 mm., the actual length used being read off on the vernier and scale. In filling the tube the funnel is removed, the plug inserted in its place, the tube drawn out to its full extension and filled in the usual way by removing the end cap. The tube is next placed vertically, the funnel is replaced and the tube shortened to drive a little solution into the funnel. After placing the tube horizontally a few ml. of solution are added to the funnel and the cap is fitted to prevent evaporation.

Landolt gives the following table (1) for solutions to be used in checking the Ventzke scale :

TABLE 1

Grams of sucrose in 100 ml. of solution	Starting-point for verification	Range of scale divns. : for verification
12·53	100 V	95.90 ... 60.55
6·89	55	50.45.40.35.30
3·76	30	25.20.16
2·00	16	15.10.9
1·13	9	5

The sugar must be purified before use. The International Committee's method is the following : The purest commercial sucrose is used to prepare a hot saturated aqueous solution. This is precipitated with absolute ethyl alcohol (acid free), spun in a small centrifuge and washed therein with absolute alcohol. The crystals so obtained are redissolved and re-precipitated a second time. The second crop of crystals is dried between filter paper and preserved in a glass vessel. The moisture present is determined by drying *in vacuo* at 70° for 4 hours, and allowance is made for this in the calculation of the concentration of the solutions.

In using the control tube, a solution is made up having a concentration of 12·53 grams of dry sugar in 100 ml. at 20°. The scale of the saccharimeter is set at exactly 100° and the tube placed in position. The length of the tube is adjusted until equality of field is obtained and the length of the tube is read off from the vernier and scale. The number of degrees can then be calculated and compared with the scale reading. The setting is repeated a number of times and the average value taken for the calculation. The saccharimeter scale is next set at 95°, and the above procedure repeated, and so on throughout the scale. The 100° point having been verified by means of a control plate, it can be taken to standardize the solution. Thus, if the length of the tube for two points were

$$100° \text{ V} \qquad . \qquad . \qquad . \qquad . \qquad 396\cdot365 \text{ mm.}$$
$$95° \text{ V} \qquad . \qquad . \qquad . \qquad . \qquad 376\cdot495 \text{ mm.}$$

then

396·365 mm. correspond to 100°

$$\therefore 1 \text{ mm. corresponds to } \frac{100°}{396\cdot365}$$

and

$$376\cdot495 \text{ mm. corresponds to } \frac{100 \times 376\cdot495}{396\cdot365} = 94\cdot987°$$

i.e. if the 100° scale division is correct the 95° scale division corresponds to 94·987° V. The first solution is used down to 55° and the value of this scale reading is taken in terms of the 100° scale reading. The value so obtained is used to determine the strength of the second solution.

For the determination of sucrose in brown sugar or other products a double polarization method has been devised by Jackson and Gillis.[1]

Temperature Corrections. When quartz wedge saccharimeters are used at temperatures other than 20° temperature corrections must be applied. The rotation for quartz is given by

$$\alpha_t^D = \alpha_{20}^D \{1 + 0\cdot000143(t - 20)\}$$

and since the expansion coefficient of quartz parallel to the optic axis is 0·000007, the specific rotation coefficient becomes 0·000136. The linear expansion coefficient of quartz perpendicular to the optic axis is 0·000013, and that for the nickelin scale on the wedge is 0·000018, so that the total temperature coefficient becomes

$$0\cdot000136 + 0\cdot000007 - 0\cdot000013 + 0\cdot000018 = 0\cdot000148.$$

[1] United States Bureau of Standards Paper No. 375, 1920.

If the scales are etched on the wedges the scale coefficient becomes zero, while if they are on glass it is 0·000008. Hence the true polarization (S_{20}) of a solution is given by

$$S_{20} = S_t\{1 + 0{\cdot}000148(t - 20)\}.$$

When checking with the quartz plate the corrected reading is

$$T_{20} = T_t\{1 + 0{\cdot}00005(t - 20)\}.$$

The rotation of sucrose is also dependent on the temperature (and on the concentration). For a normal solution made up and polarized at $t°$ the polarization in sugar degrees at 20° is given by

$$V_{20} = V_t\{1 + 0{\cdot}0003(t - 20)\}.$$

If the solution is made up at 20° and is polarized at $t°$ in a glass tube, then

$$S_{20} = S_t\{1 + 0{\cdot}000609(t - 20)\}.$$

Saccharimeter with Sodium Light. With the electric sodium lamp introduced by Messrs. Bellingham & Stanley, Ltd.,[1] a suitable source of monochromatic light is now available for use with saccharimeters without the quartz wedge device. It only differs from the polarimeter in being provided with a sugar scale reading from − 30 to + 110 International Sugar Degrees. The scale is etched on a glass circle and requires no magnification. The vernier attachment also is etched on a glass plate. The elimination of the quartz wedge obviates any error due to want of optical homogeneity of the quartz. It renders also unnecessary the exact adjustment of the temperature of the apparatus to that of the observation tube.

The reading is taken not by reflected but by transmitted light.

[1] *Nature*, 1937, 678.

SECTION 3 : REFRACTION

Introduction. The determination of the refractive index of liquids is not only of academic importance, but also of considerable use in the examination of animal and vegetable oils and fats, essential oils, aqueous and alcoholic solutions, and in the case of a number of technical liquids. The measurements are so readily made and the quantity of material required is so small that the determination compares favourably with that of the specific gravity.

The most important refractometers used in physico-chemical laboratories are :

1. The Abbe refractometer.
2. The Zeiss butyro-refractometer.
3. The Pulfrich refractometer.
4. Amagat and Jeans' oleo-refractometer.
5. The Féry refractometer.
6. The Dipping refractometer.
7. The Rayleigh interference refractometer.

The Abbe Refractometer is shown in Fig. 11 (VI *). The range of the instrument is from 1·3000 to 1·7000, the maximum accuracy attainable being 0·0001. Among the advantages of the Abbe are the fact that a single drop only of the liquid is required, either daylight or artificial light can be used, the refractive index is read off directly from the scale, the dispersion can be measured if desired, and the temperature regulated.

With regard to temperature regulation, most vegetable oils are found to have a temperature coefficient of refractive index of 0·000365 per degree Centigrade, so that an accuracy of 0·2° in temperature regulation is sufficient, and the thermometer supplied with the instrument is accurate to this extent.

Principle of Refractometer. The principle of this refractometer is illustrated in Figs. 12 (VI *) and 13 (VI *), where the former shows the test piece of glass T in position on the prism P_2, and the latter shows a film of oil dc between the two prisms P_1 and P_2. White light passing along ab is reflected by the mirror M into the prism P_1; the face AB of this prism has a matte surface which scatters the light entering the oil film c between the two prisms. The critical ray is cdeF; this is the ray grazing the surface CD of the prism P_2. The value of the angle θ and also of the angle i will depend therefore on the refractive index of the oil and on that of the prism; the latter being a constant. When the emergent rays are brought to a focus by means of the telescope they will all lie on one side of a line in the focal plane. The field therefore will be divided into a bright and a dark portion by a straight line. If white light were used this boundary would not be sharp, but would be coloured owing to

the refractive indices, and therefore the critical angles, being different for light of different wave-lengths. This difficulty is overcome by mounting two direct-vision prisms, one above the other, in front of the object glass of the telescope ; these prisms can be turned in opposite directions by means of a milled head, the degree of rotation being indicated on a circular scale. In the first instance let these prisms be situated so that their dispersion planes and that of the prism P_2 are parallel, and the dispersion of the two compensating prisms is in the same direction. If the dispersion for the C and F lines produced by a single prism is d, that produced by the two in conjunction will be $2d$. If now the milled head be turned so as to rotate the compensating prisms in opposite directions through an angle of 90°, the total dispersion will become zero ; and if through a further 90° it will become $-2d$. A position can thus be found
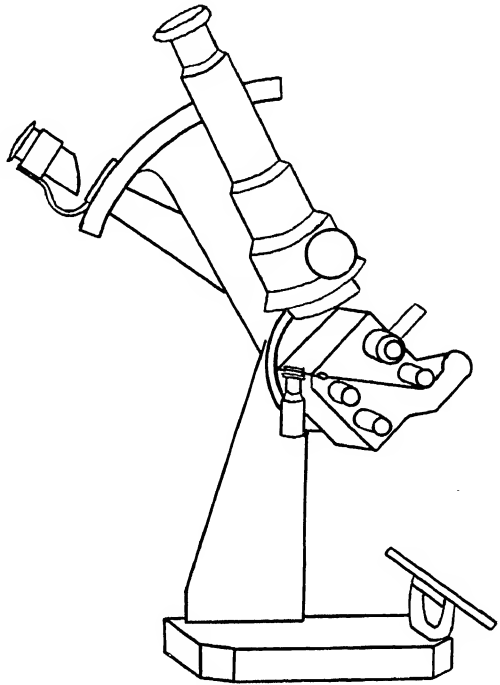
FIG. 11 (VI*)

where the dispersion produced in the prism P_2 is just compensated by that of the two direct-vision prisms and the edge of the field then becomes sharp and colourless. At the same time the position of the compensating prism gives an approximate value for the dispersion, a table being supplied with the instrument to give the relation between the dispersion and the scale reading. The
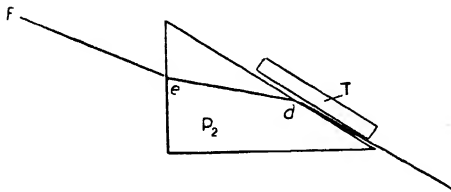
FIG. 12 (VI*)
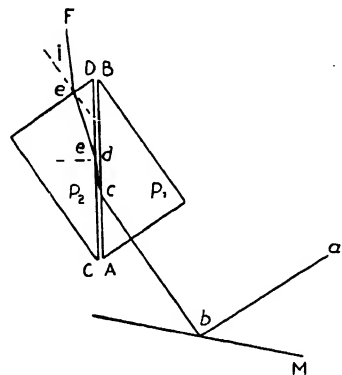
FIG. 13 (VI*)

prisms P_1 and P_2, which are of dense flint glass, are mounted in water jackets through which a stream of water at constant temperature is circulated. The mountings of the two prisms are hinged at one end and fastened at the

other by turning a milled head, so that a thin film of the liquid can be enclosed between them. The bulb of a thermometer projects into the upper jacket and gives the temperature of the issuing water. The prism system is attached to an arm which carries the reading lens and an index which moves over the scale, which is graduated to read refractive indices; the prisms and arms rotate about a horizontal axis. The telescope containing the compensating prisms is attached to the sector on which the refractive-index scale is engraved and can also be turned about a horizontal axis.

Use of Instrument. The instrument is used as follows : The refractometer having been placed in front of a window, the thermometer is inserted and the water circulation started. Both the arms are moved right forward and the milled head is turned to separate the prisms; by holding the prism arm in the left hand the surface of the upper prism is maintained in a horizontal position. A drop of the oil is placed on the polished surface by means of a glass rod and is spread over the surface; the lower surface is then turned over and clamped. The sector arm is next turned over until it touches the back stop and the position of the mirror is adjusted so that the light enters the telescope. The eyepiece is focused on the cross-wires and the reading lens on the scale ; on moving the prism arm a position can now be found where the lower part of the field is dark and the upper part light. In general, the border-line will be found to be coloured, and this is corrected by turning the milled head on the right of the telescope, which operates the compensating prisms until the colour disappears and a sharp black-to-white edge is obtained. The prism arm is now moved until this black edge just crosses the intersection of the cross-wires ; the refractive index can then be read off on the scale, the fourth figure after the decimal point being obtained by estimating to one-tenth of a scale division. The temperature is recorded, as is also the reading on the dispersion scale. As soon as possible the oil should be removed from the faces of the prisms by means of a swab of cotton wool soaked in ether or ether-alcohol, the swab being renewed two or three times. The lower prism may be cleaned with a piece of linen, but the surface of the upper prism requires to be treated with particular care to prevent scratching the surface of the soft glass. Checking the accuracy of the refractive-index scale is done by means of a small test piece of glass supplied with the instrument. This test piece has two polished surfaces at right angles ; the larger face is attached to the upper prism P_2 by means of a drop of liquid of high refractive index, as, for example, monobromonaphthalene, the two prisms being opened for the purpose and the test piece being fixed parallel and as close as possible to the edge of the prism remote from the telescope. The light entering the small edge of the test piece may be diffused by means of a piece of tissue paper, or, in a good light, the opposite end of the test piece which is left greyed may be used. The compensator is set and the reading on the refractive-index scale is noted and compared with the value etched on the test piece. Errors may be corrected by means of the small steel adjusting screw on the back of the telescope, i.e. on the side nearer the lower refractive-index end of the scale.

Temperature Correction. In work of the highest precision the temperature effect on the prisms is taken account of. The correction to be added amounts to approximately one unit in the fourth place for a rise of 15° of the compensating prisms, and of from 7° to 22° of the Abbe prisms above the standard temperature. The correction is calculated from the formula

$$R = r_1(t_1 - 20) + r_2\eta(t_2 - 20)$$

where R is the number of units in the fifth place to be added, r_1 and r_2 are obtained from Table 1 given below, t_1 is the temperature of the Abbe prism, and t_2 that of the compensating prisms.

TABLE 1

Refractive index							r_1		r_2
1·30	.	.	.	.	.	.	0·68	.	1·56
1·40	.	.	.	.	.	.	0·67	.	1·39
1·50	.	.	.	.	.	.	0·67	.	1·18
1·60	.	.	.	.	.	.	0·67	.	0·91
1·70	.	.	.	.	.	.	0·70	.	0·46

In a similar way the correction for the dispersion is obtained from the equation

$$S = (s_1 + \sigma\mu)(t_1 - 20) + s_2\mu(t_2 - 20)$$

s_1, s_2 and σ being obtained from Table 2, being the number of units in the fifth decimal place to be added to the dispersion already found.

TABLE 2

Refractive index					σ		s_1		s_2
1·30	.	.	.	.	0·02	.	0·31	.	1·00
1·40	.	.	.	.	0·02	.	0·30	.	0·92
1·50	.	.	.	.	0·03	.	0·30	.	0·79
1·60	.	.	.	.	0·05	.	0·31	.	0·60
1·70	.	.	.	.	0·09	.	0·32	.	0·27

Temperature Control of the Prisms. The refractive index at 40° is the value now generally recorded in the literature of fats and oils, so that for precision work the prisms and the film of oil between them are heated up to this temperature. For work of a lower degree of accuracy the refractive index can be determined at another temperature and calculated to 40° by making use of the fact that the refractive index of most animal and vegetable oils decreases 0·000365 per degree. Temperature regulation to 0·1 or 0·2 of a degree is evidently sufficient and the heating water may either be pumped through the prisms (leaving by the tube near the thermometer bulb) from a thermostat, or one of the devices used with other forms of refractometer can be used. One such device consists of a constant-level water-bath attached to the wall above a water-tap; the water passes from this vessel through a metal spiral immersed in a water-bath heated by a gas burner and then to the refractometer; by adjustment of the gas and water supply temperature regulation of the degree required can readily be obtained.

The Zeiss Butyro-refractometer has a pair of jacketed Abbe prisms, the upper prism being fixed to the telescope, as shown in Fig. 14 (VI *), and the telescope being rigidly fixed to the base. The instrument is used in the same way as the Abbe instrument, but differs from the latter in that there are no compensating prisms to counterbalance the dispersion,

this being corrected for one value of the dispersion only, namely that of butter-fat. The upper prism is arranged so as to give just the opposite dispersion to the rays leaving its upper surface to that caused by the butter-fat between the prisms. The result of this is that the edge is coloured either blue or red with all other substances, but at the same time the edge is not rendered so indistinct as to prevent readings being taken exactly over the range of the instrument, which is from 1·418 to 1·492 (the Abbe range being 1·3 to 1·7). A scale graduated from − 5 to + 105 is placed in the focal plane of the telescope objective and the upper lens of the ocular is adjustable so as to enable the scale to be brought into focus. The water circulation
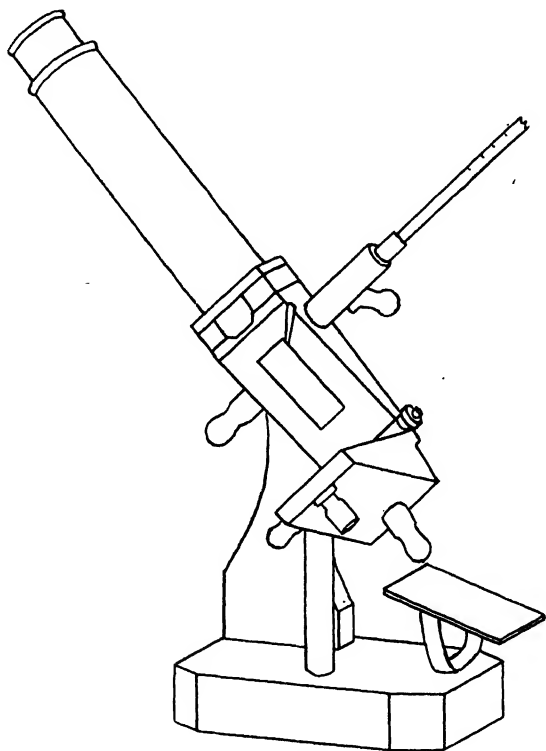
FIG. 14 (VI *)

having been started, the whole instrument is turned up on its side while the oil is applied to the upper prism and the prisms are closed. In a few moments, when the temperature of the film has become constant, the field will be seen to be separated into two parts by a vertical line, being dark on the right and light on the left, the dividing line itself being in most cases somewhat coloured (any want of definition may be due to air bubbles in the film). The eyepiece is focused on the scale and the position of the dividing line on the scale read off, tenths of a division being obtained by rotating the micrometer screw until the border-line coincides with a scale division, when the drum reading gives the number of tenths to be added to the scale reading. The temperature coefficient of the refractive index of butter-

fat is 0·55 scale divisions per degree Centigrade. The butyro-readings can be converted to refractive indices by the table.

Scale reading		Refractive index
0	. . . .	1·4220
10	. . . .	1·4300
20	. . . .	1·4377
30	. . . .	1·4452
40	. . . .	1·4524
50	. . . .	1·4593
60	. . . .	1·4659
70	. . . .	1·4723
80	. . . .	1·4783
90	. . . .	1·4840
100	. . . .	1·4895

Checking Scale Readings. The scale reading can be checked from time to time by means of the standard liquid supplied by the makers, and in case a deviation of more than one or two tenths of a division is shown an adjustment can be made in the following way. The standard liquid gives the border-line at

Temp.			Temp.			Temp.		
8°	. . . . .	81·6	14°	. . . . .	77·9	20°	. . . . .	74·3
9	. . . . .	81·0	15	. . . . .	77·3	21	. . . . .	73·6
10	. . . . .	80·4	16	. . . . .	76·7	22	. . . . .	73·0
11	. . . . .	79·8	17	. . . . .	76·1	23	. . . . .	72·4
12	. . . . .	79·2	18	. . . . .	75·5	24	. . . . .	71·8
13	. . . . .	78·6	19	. . . . .	74·9	25	. . . . .	71·2

The nut G (Fig. 15 (VI *)) is eased and the milled disc (not lettered) is turned till the border-line stands on the required integral number; the black drum F is then turned till the index coincides with the number of tenths required by the standard liquid; the nut G is tightened up and the accuracy of the reading again checked.

The Pulfrich Refractometer measures the refractive indices of liquids and solids with an accuracy of 0·0001 and dispersion to approximately 0·00002.

Theory. Let μ_1 be the refractive index of the substance under examination,

and μ_2 be the refractive index of the prism II (Fig. 16 (VI *)),

and i be the angle of emergence.

FIG. 15 (VI *)

The ray AB is the glancing ray at the interface between I and II. At B we have

$$\frac{\sin 90}{\sin (90 - r)} = \frac{\mu_2}{\mu_1}$$

At C

$$\frac{\sin i}{\sin r} = \mu_2$$

hence $\mu_1 = \sqrt{\mu_2{}^2 - \sin^2 i}$, the angle i being the one to be measured,
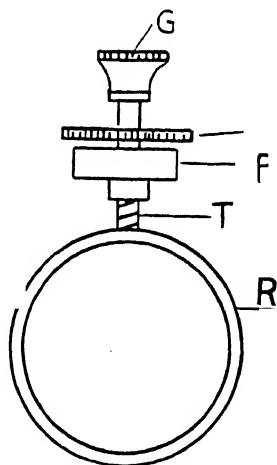
Use of Instrument. The prism II has a refractive index greater than
that of the liquid whose refractive index is to be measured and has two
plane polished surfaces at right angles ; that these two surfaces are really
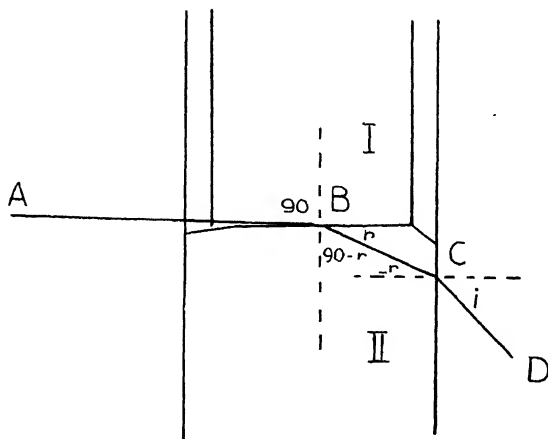
FIG. 16 (VI *)

at right angles is first tested. One of the surfaces is horizontal, and on it
is fixed the substance under examination if this be a solid, or a cylindrical
glass cell containing the substance if the latter be a liquid. Light from,
for example, a hydrogen tube S (Fig. 17 (VI *)) passes through the con-
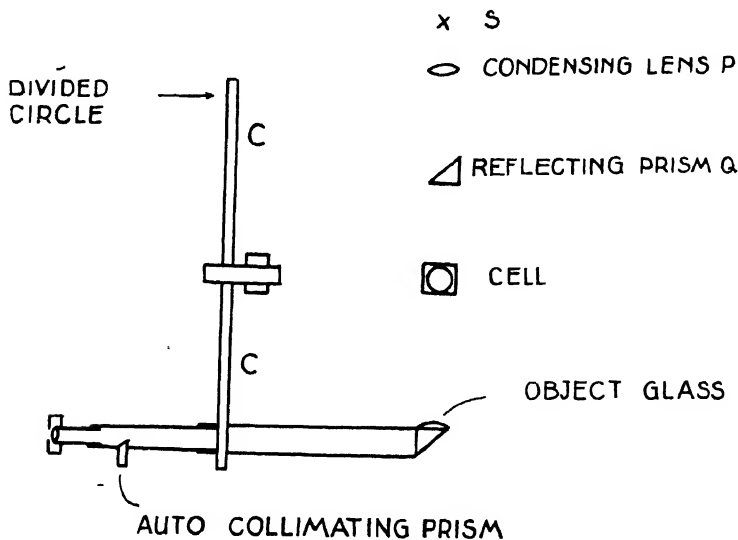
AUTO COLLIMATING PRISM
FIG. 17 (VI *)

densing lens P and into the cell almost horizontally, so that it enters the
prism II at the glancing angle. The emergent beam will then be bounded
by the ray which just grazes the surface. The position of the sharp edge
is observed by means of the telescope attached to the divided circle CC ;
on this circle the angle i can be read by means of a vernier to one minute.

For dispersion measurements the drum can be clamped and a micrometer screw used; one division on this drum of the screw is equal to six seconds of arc. The prism and cell are jacketed so that the temperature can be controlled with accuracy. The lines usually measured are C, F and G from the hydrogen spectrum, and D from a sodium flame; the last is conveniently brought into the field by means of the small reflecting prism Q. In taking readings for dispersion purposes the tangent screw is brought near the beginning of its range and the telescope is turned until the C line occupies the middle of the field. The divided circle is then clamped and the position of the four lines fixed by means of the tangent screw. When using the instrument with solids the solid must have two polished faces approximately at right angles, and one of these should be from 2 to 3 cm. long and be accurately flat to give good contact with the top of the prism II. The solid is attached to II by means of a film of oil having a refractive index greater than that of the specimen I. The fact that the surfaces of I and II are parallel can be verified by observation of the interference bands in the film of oil.

Amagat and Jeans' Oleo-refractometer differs from the previous instruments in that it measures the difference in refractive index between

FIG. 18 (VI *)

two liquids. As shown in Fig. 18 (VI *) it consists of a collimator, a telescope and a metal vessel. The metal vessel is surrounded with a larger vessel to contain water and act as a thermostat; the water is heated by means of a lamp, the temperature being indicated by a thermometer. The metal vessel is fitted with parallel plate-glass windows so that light from

an ordinary gas jet passes through the collimator, then through the metal vessel by means of the windows, and finally into the telescope. Inside the metal vessel is a small silver cylinder whic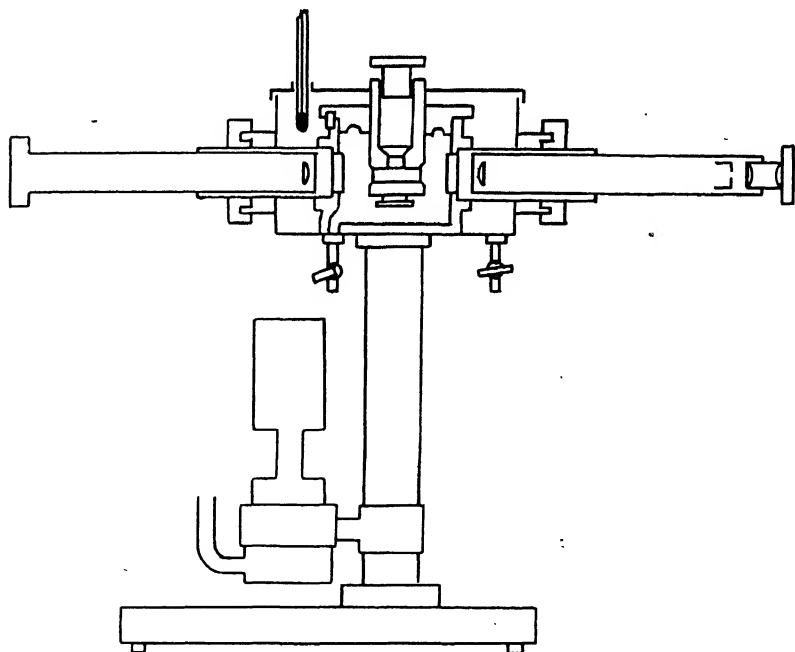h is hollow and is provided with two plate-glass windows inclined at an angle of 107°. At the focus of the telescope eyepiece is fitted a scale and in the collimator is a semi-circular stop. When the silver cylinder and the outer metal vessel are filled with the same oil there is no refraction, so that the image produced by the edge of the stop in the collimator is not altered in position by filling the two vessels with oil. But if the refractive indices of the liquids in the cylinder and the trough differ from one another there will be refractions so that the image of the edge of the stop will be displaced along the scale. With the instrument is supplied a standard oil (huile type), the composition of which is kept secret, but which is said to be sheep's-foot oil (Lewkowitsch). This oil is heated to 22°, and both receptacles are filled with it; the outer water-jacket having been previously regulated to 22°. All the reservoirs having been filled and having attained the temperature 22°, the position of the dark edge on the scale is observed, and if this is not at the zero of the scale it is brought there by adjusting the position of the shutter in the collimator. The oil in the middle cylinder is then run out by means of the tap at the bottom, and the oil to be examined, having been heated to 22°, is used first to wash out the inner cylinder and then to fill it. If now the refractive index of this oil be different from that of the standard oil in the metal vessel, the position of the dark edge on the scale will be altered. The obvious advantage of the instrument is that it allows of a very accurate comparison of two oils.

The **Féry Refractometer** is shown in Fig. 19 (VI *), and can be used for liquids having refractive indices between 1·3300 and 1·6700. This instrument consists of a collimator and a telescope fixed coaxially on a

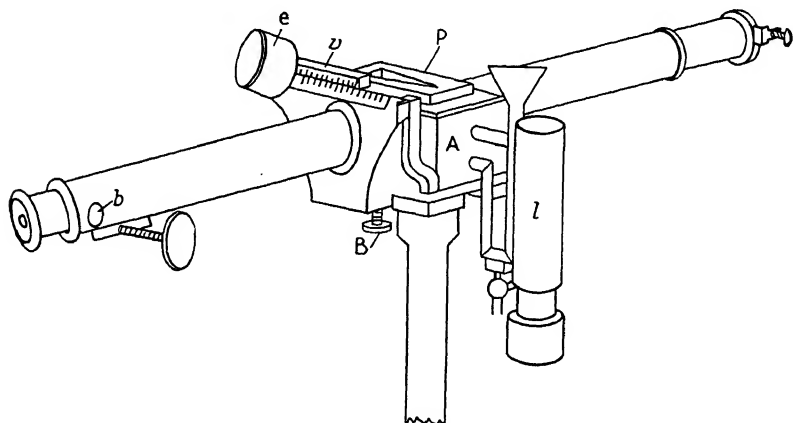FIG. 19 (VI *)

stand and having a space between them in which rides horizontally, and at right angles to the axis of the telescope, a metal box A. The carrier of this box A is moved by a rack and pinion operated by the thumb-screw B, and has attached to it a thermo-siphon heater *l* and a vernier and lens

v and e. The vernier moves over the scale of refractive indices which is attached to the fixed frame of the apparatus. The two longer walls of A are formed of cylindrical plano-convex lenses, having the plane surfaces towards the inside of the box. Attached to the frame of the apparatus is a holder (not shown in the figure) capable of movement in a vertical direction, and to which is attached the metal box p. This box is rectangular and contains glass wedges arranged as shown in Fig. 20 (VI *), leaving a prismatic opening G in which the liquid is to be placed. The bottom of p consists of a block of glass, and a removable top of glass, having a hole for the thermometer, forms the cover. In the metal cover of p are two windows, one of which allows light to pass through the glass bottom of the box and the other through the prism of liquid G.

Use of Instrument. The instrument is used thus : The box A and the cavity G are filled with distilled water, the cover and thermometer having been fitted to p. This box is placed in its holder and is lowered into the water in A and the slotted cover of A is put in place. The rectangular aperture of the collimator is movable by means of a screw
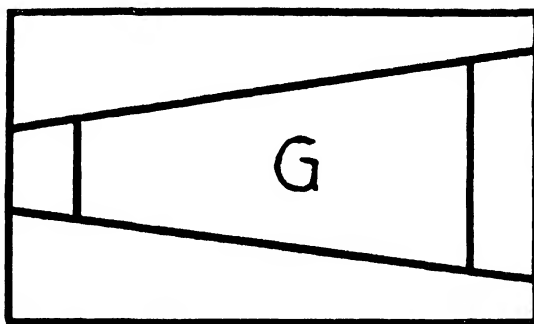
FIG. 20 (VI *)

and carries two lines marked 0 and 1, corresponding to two lines similarly marked on the head of the collimator. The two lines marked 0 are brought into coincidence and the aperture is illuminated with sodium light. The refractive index of the glass of which the bottom of the box p is made is marked on the instrument and may be, for example, 1·51284 ; the vernier is set on this figure by moving the box A by means of the nut B. The eyepiece of the telescope is then focused on the cross-wires, and on looking through the telescope an image of the slit will be seen in the form of a vertical yellow line. This line is next brought into focus by means of a screw, and then the cross-wires are moved by means of the screw b until the yellow line passes through their intersection. A second image of the slit will be formed by the light which passes through the upper window and hence through the prism G containing distilled water ; refraction takes place here, so that the image does not fall on the intersection of the cross-wires. If, however, the box A is moved by means of the thumb-screw B, the sides of the box A, which effectually consist of a prism pair of gradually increasing angle, will at length bend back the ray refracted in G until it also passes through the intersection of the cross-

wires. The position of the vernier on the scale when this is the case is marked with the refractive index of water corresponding to the temperature of the experiment, and thus the correctness of the scale can be verified by reference to the following table :

Temp.	Refractive index	Temp.	Refractive index
0°	. 1·33402	20°	. 1·33303
5	. 1·33392	25	. 1·33255
10	. 1·33373	30	. 1·33200
15	. 1·33344		

To obtain the refractive index of any other liquid the box is removed, the new liquid placed in the cavity G and the box replaced. The correctness of the image produced by the glass is again verified and the screw B then turned until the image produced by the liquid in the cell intersects the cross-wires, when the refractive index can be read off directly on the scale and vernier. For liquids having a refractive index above 1·59 the procedure to be followed is the same, with the exception that the slit on the collimator is moved so that the lines marked 1 are brought into coincidence instead of the lines marked 0. The effect of this is that all the scale readings are to be increased by 0·14, and the scale is virtually extended to 1·7300. In setting for the ray passing through the glass the vernier is therefore set on reading 1·3728, instead of on 1·5128, and should the liquid ray reading on the scale be, for example, 1·5827, the refractive index would exceed this by 0·14 and would be 1·6227. When readings of the refractive index are to be taken at a temperature above room temperature, the small lamp on the thermosiphon is lighted, the temperature indicated by the thermometer is observed, and when this has risen to 0·5° of the de-
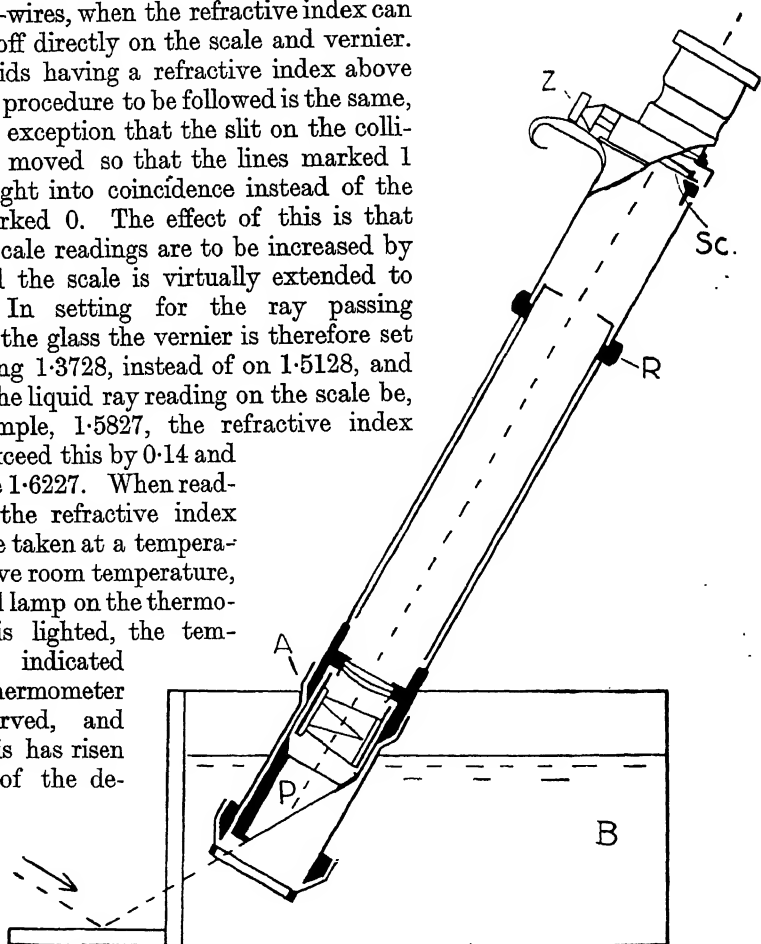

FIG. 21 (VI *)

sired temperature the lamp is turned out. The temperature then slowly rises to the required value when the reading of the scale is taken.

The Dipping Refractometer (Fig. 21 (VI *)) is extremely useful in the examination of dilute aqueous solutions whose refractive indices lie between 1·3254 and 1·3664. It has been applied in the analysis of fermented liquors (beers) and recently to the examination of milk. The instrument consists of a telescope having a hard glass prism of refracting angle about 63°, fixed at its lower end and containing a compensator A, a scale Sc, and micrometer screw Z. The hard glass prism dips into a beaker containing the solution under examination; the rays entering the prism at the glancing angle are corrected for colour by means of the compensating prism and are brought to a focus on the scale, so that the position of the border-line between the light and the dark parts of the field enables the refractive index, or rather the scale reading corresponding thereto, to be read off. A heating trough B is provided with holes for the support of small glass beakers to contain the solutions, a support for the instrument and a mirror to reflect white light up through the trough.

Manipulation. The correctness of the instrument is first checked by putting distilled water into one of the beakers, and ten minutes are allowed for temperature equilibrium to be attained. The eyepiece is then focused on the scale by rotating it, the mirror is adjusted to throw the light through the bottom of the beaker, and the border-line is made sharp by turning the compensator by means of the milled ring R. The scale is divided from − 5 to + 105, and the whole number of scale divisions is noted down; the micrometer screw Z is then turned, sliding the scale towards the border-line until a scale line coincides with the former, when the index of the micrometer drum shows the decimals of a scale division to be added. An error of 0·1 scale divisions is equivalent to an error of 3·7 units in the fifth decimal place of the refractive index. The following table gives the reading of the scale for water for various temperatures :

Temp.	R.I.	Temp.	R.I.	Temp.	R.I.
10°.	16·3	17·5°	15·0	24°.	13·5
11	16·15	18	14·9	25	13·25
12	16·0	19	14·7	26	13·0
13	15·85	20	14·5	27	12·7
14	15·7	21	14·25	28	12·4
15	15·5	22	14·0	29	12·1
16	15·3	23	13·75	30	11·8
17	15·1				

If the average of several readings shows an error of more than 0·1 scale divisions the scale must be readjusted as follows : While the instrument hangs on the wire frame the micrometer drum is set to 10, the steel spike to be found in the case of the apparatus is inserted into one of the holes of the cross-holed screw lying on the inner side of the micrometer drum, and the spike is turned anti-clockwise as seen from the rear, so loosening the nut. The spike is then turned until the border-line just corresponds to the correct scale integral reading for water at the temperature of the experiment, and the drum is turned to give the correct decimal number. The drum is then held firmly in position and screwed up tight, and the correctness of the reading is again checked. The temperature of the bath can be maintained constant by a flow of water through it from one of the heating devices already described. Solutions in volatile

solvents can be examined by means of a metal beaker adapted to fit the prism end of the instrument. The refractometer is inverted and the beaker fixed in position by means of the bayonet joint. The solution is poured in to fill the beaker completely and the cap is placed on and locked in position. The metal beaker is then placed in the bath and the reading taken in the usual way. When only small quantities of liquid are available an auxiliary prism is used. The metal beaker is first fixed on the inverted telescope ; a few drops of the liquid are then placed on the hypotenuse face of the auxiliary prism, which is held horizontally for this purpose, and this face is then placed in contact with the face of the telescope prism within the beaker and is secured in position by fixing the cover of the beaker ; sufficient liquid should be used just to fill the space between the faces of the two prisms. The measurement is then made in the usual way. The relation between scale reading and refractive index is given in the table :

Scale	R.I.	Scale	R.I.	Scale	R.I.	Scale	R.I.
−5	.. 1·32539	23	.. 1·33625	51	.. 1·34687	79	.. 1·35714
−4	.. 2578	24	.. 3667	52	.. 4724	80	.. 5750
−3	.. 2618	25	.. 3705	53	.. 4761	81	.. 5786
−2	.. 2657	26	.. 3743	54	.. 4798	82	.. 5822
−1	.. 2696	27	.. 3781	55	.. 4836	83	.. 5858
0	.. 2736	28	.. 3820	56	.. 4873	84	.. 5894
1	.. 2775	29	.. 3858	57	.. 4910	85	.. 5930
2	.. 2814	30	.. 3896	58	.. 4947	86	.. 5966
3	.. 2854	31	.. 3934	59	.. 4984	87	.. 6002
4	.. 2893	32	.. 3972	60	.. 5021	88	.. 6038
5	.. 2932	33	.. 4010	61	.. 5058	89	.. 6074
6	.. 2971	34	.. 4048	62	.. 5095	90	.. 6109
7	.. 3010	35	.. 4086	63	.. 5132	91	.. 6145
8	.. 3049	36	.. 4124	64	.. 5169	92	.. 6181
9	.. 3087	37	.. 4162	65	.. 5205	93	.. 6217
10	.. 3126	38	.. 4199	66	.. 5242	94	.. 6252
11	.. 3165	39	.. 4237	67	.. 5279	95	.. 6287
12	.. 3204	40	.. 4275	68	.. 5316	96	.. 6323
13	.. 3242	41	.. 4313	69	.. 5352	97	.. 6359
14	.. 3281	42	.. 4350	70	.. 5388	98	.. 6394
15	.. 3320	43	.. 4388	71	.. 5425	99	.. 6429
16	.. 3358	44	.. 4426	72	.. 5461	100	.. 6464
17	.. 3397	45	.. 4463	73	.. 5497	101	.. 6500
18	.. 3435	46	.. 4500	74	.. 5533	102	.. 6535
19	.. 3474	47	.. 4537	75	.. 5569	103	.. 6570
20	.. 3513	48	.. 4575	76	.. 5606	104	.. 6605
21	.. 3551	49	.. 4612	77	.. 5642	105	.. 6640
22	.. 3590	50	.. 4650	78	.. 5678		

The Rayleigh Interference Refractometer (Fig. 22 (VI *), which does not show the collimator) is used for measuring the small difference in refractive index between two gases. Fig. 23 (VI *) shows a vertical section, Fig. 24 (VI *)A shows a horizontal section through XY, and Fig. 24 (VI *)B shows a horizontal section through VW. Light from a vertical slit A (Fig. 24 (VI *)B) is collimated by the achromatic lens B, and then passes through two vertical parallel slits C, 12 mm. apart. The lower half of each beam (Fig. 24 (VI *)A) now passes through a gas tube 100 cm. long (D and E), and then through a thin glass plate inclined at 45° to the optical

axis. One plate (K) is fixed, the other (L) is movable so that the optical
path of the beam can be altered. The upper halves (Fig. 24 (VI *)B) of
the two beams pass in the air to a thick glass plate H which bends them
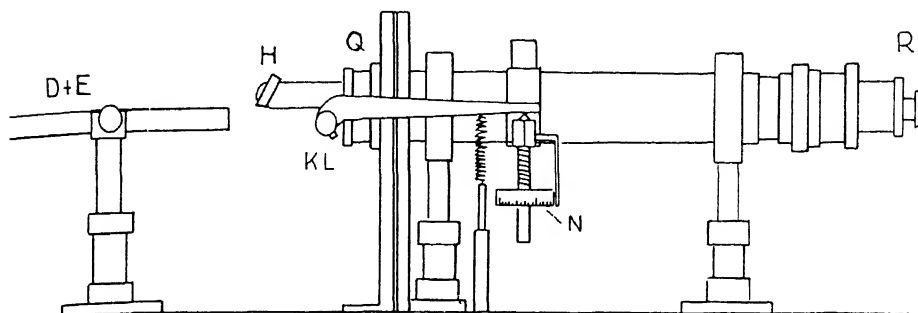
FIG. 22 (VI *)

down so that their lower edges coincide with the upper edges of those parts
of the beam which pass through the gas tubes. The rays are next brought
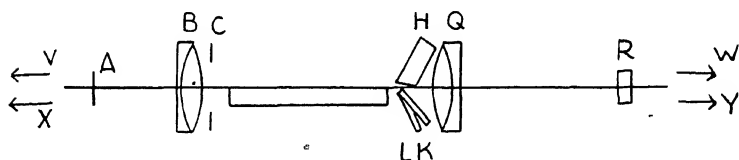
FIG. 23 (VI *)

to a focus by the achromatic lens Q. The two beams passing through the
air are of fixed paths and so give a fixed interference system of reference.
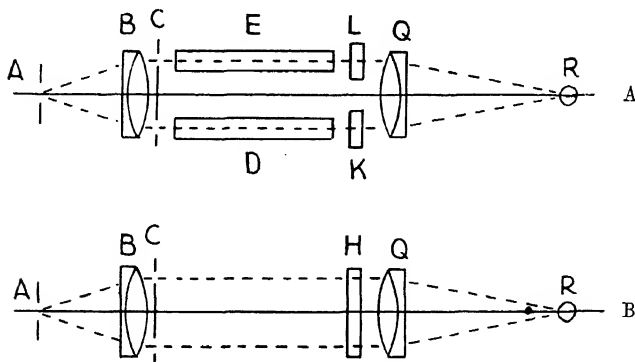
FIG. 24 (VI *), A and B

The optical lengths of the paths through the two gas tubes depend on the
nature, temperature and pressure of the gases and on the position of the
plate L. The interference bands produced by the upper and lower systems
are viewed by means of the cylindrical lens R ; two systems of interference

bands are seen, one above the other. The angle of the plate L is then altered by turning the screw attached to the drum N, which moves against a spring plunger a lever attached to L, until the two series of bands coincide. The reading of the micrometer drum is now the zero of the instrument. When a gas of slightly different refractive index is placed in one of the gas tubes the lower series of bands will be displaced slightly; it is brought back to coincidence by means of the nut N, and the reading of the drum is again taken. The difference of the two readings will depend on the difference of the refractive indices of the two gases in the tubes. One division of the drum corresponds to a movement of the plate L through two and a half seconds, and to a shift of the bands of about 0·0083 of a band. Settings can be repeated with an accuracy of 0·025 of a band or three divisions of the micrometer scale. The minimum quantities of gases detectable in air by this is illustrated in the table.

|										
Hydrogen .	.	.	.	.	.	.	.	.	0·01	per cent
Helium .	.	.	.	.	.	.	.	.	0·006	,, ,,
Argon .	.	.	.	.	.	.	.	.	0·15	,, ,,
Water .	.	.	.	.	.	.	.	.	0·04	,, ,,
Chlorine .	.	.	.	.	.	.	.	.	0·003	,, ,,
Carbon dioxide .	.	.	.	.	.	.	.	.	0·0095	,, ,,

Calibration of Instrument. The instrument has been used to measure the permeability of balloon fabrics to hydrogen and to estimate the carbon dioxide in flue gas. It can be calibrated by filling both tubes with dry air at a definite temperature and pressure, and then progressively varying the pressure in one tube and noting the scale reading corresponding to each pressure. The difference in refractive index is given by

$$\Delta\mu = \frac{273 \times 0\cdot0002926(p_1 - p_2)}{760T}$$

where p_1 and p_2 are the pressures in the two tubes and T is the absolute temperature of the experiment. (The refractive index for dry air at 0° and 760 mm. is taken as 1·0002926.)

The Rayleigh type of interference refractometer is suitable for the estimation of small quantities of gases (e.g. 0·2 per cent carbon monoxide) in air.

For measuring refractivities, it is claimed that in point of accuracy the interferometer is superior to all other instruments. As an example of an extreme case where small difference in the refractive index might be expected the case of deuterium might be mentioned. Orr [1] uses a Rayleigh gas interferometer to measure the difference in the refractive indices of H_2 and D_2. Assuming the value 1·00013966 for H_2 at $\lambda5462$, he found the refractive index of D_2 to be 1·0001378(7).

Instrument for Use with Liquids. A similar instrument is made for use with liquids. The gas tubes are replaced by a glass cell 1 cm. (or 10 cm.) long, the body of which is a solid piece of glass. The two openings for the liquids are in the upper half of the block, so that the variable interference bands are here above the fixed comparison bands. The plates K and L are thicker, so that the range of refractive-index difference for

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[1] *Trans. Far. Soc.*, 1936, **32**, 1556.

liquids is 0·008 instead of 0·000017 as for gases.   The two compartments of the cell are each provided with a thermometer.   The beam passes through the lower part of the liquid in the cell so as to avoid surface effects such as difference of temperature or concentration.

Refractive Indices (μ_D) of some organic liquids for the sodium D line ($\lambda = 5893 \times 10^{-8}$ cm.) are given below:

Alcohol methyl .	1·33	Benzene .	1·503
Ether, ethyl	1·354	Ethyl iodide	1·517
Acetone .	1·360	Ethyl salicylate	1·525
Alcohol ethyl	1·362	Canada balsam .	1·53
Alcohol amyl	1·410	Ethylene dibromide	1·542
Ethyl bromide .	1·425	Nitrobenzene	1·554
Chloroform .	1·449	Benzyl benzoate	1·572
Carbon tetrachloride	1·463	Aniline .	1·587
Olive oil .	1·46	Bromoform .	1·592
Glycerine .	1·470	Carbon disulphide .	1·631
Turpentine .	1·47	α-Bromonaphthalene	1·660
Toluene .	1·497	Methylene iodide .	1·744

The refractive indices of some solid substances (for the main D line) are as follows :

Diamond	2·42	Rock salt	1·54
Phosphorus .	2·14	Canada balsam .	1·53
Ruby . .	1·71	Felspar .	1·52
Topaz .	1·63	Fluorspar	1·43
Flint glass .	1·60	Ice	1·31

SECTION 4 : THE MICROSCOPE

The Essential Parts of a Microscope. These are the objective, the eyepiece, and the illuminating apparatus. The objective forms a real inverted and magnified image of the object as shown at 1_2 in Fig. 25 (VI *) ; the eyepiece then forms a virtual image of this at 1_4, magnifying it still further.

The Objective. Objectives are marked 1 inch, 2 inch, 4 mm., &c., these numbers indicating their equivalent focal lengths ; the 1-inch object-ive will therefore magnify more than the 2-inch, and so on. The work-ing distance of an objective is the distance between the object on which it is focused and the front of the nearest lens. Aplanatic objectives are specially corrected for spherical aberration so that a large flat field can be in focus at one and the same time.

Achromatic objectives are corrected for chromatic aberration for two colours, and generally for spherical aberration for one colour only.

Resolving Power. By the resolving power we mean that property by means of which an objective shows as two distinct and separate small elements in an object, which are very close together. The numerical aperture (N.A.) is a measure of the resolving power. The relation N.A. $= \mu \sin n$ holds between the numerical aperture, μ the lowest refractive index of any material between the object and the lowest lens, and n the angular aperture of the objective. By the angular aperture is meant the angle between the two most divergent rays from an axial point on the object which can enter the objective and take part in the formation of the image. Objectives are usually made for a tube length of 160 mm. and the draw-tube is graduated in mm. to indicate this position. To give the best results of which they are capable, dry objectives should be used with cover-slips of the particular thickness for which they have been designed. Bausch and Lomb use a thickness of 0·18 mm., and measured cover-glasses of this thickness can be obtained. A variation of 0·03 mm. in the thickness of the cover-slip will negative the correction for spherical aberration in the objective and so produce distortion. With a cover-glass that is slightly too thin the distortion can be overcome by increasing the tube length (and decreasing for a thick cover-slip) ; the compensation obtainable in this way varies with the equivalent focus and the numerical aperture of the objective ; thus with a 4 mm. 0·85 N.A. objective an increase of 30 mm. in the length of the draw-tube will balance a decrease of 0·03 mm. in the thickness of the cover-slip.

Oil Immersion. Since the numerical aperture is proportional to the lowest refractive index between the object and the lowest lens of the object-ive, and this is air in the case of a dry objective, the N.A. can be increased by replacing the air by some liquid having a higher refractive index. If

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cedarwood oil ($\mu = 1\cdot52$) is used this has practically the same refractive index as the cover-glass and the immersion is called homogeneous immersion. With oil-immersion objectives the thickness of the convex glass is
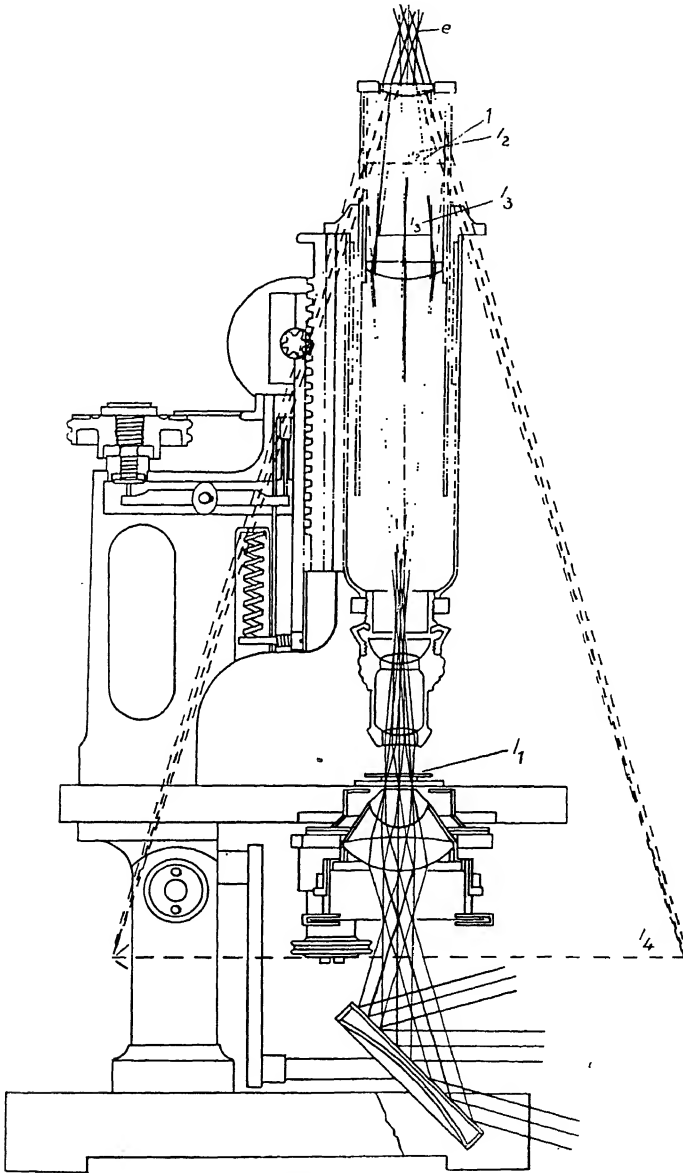

FIG. 25 (VI *)

of no importance, but the correct tube length must be adhered to strictly since a very small variation will destroy the perfection of the image. Since oil immersion increases the N.A. and so the light-grasping power as well

as the resolving power, it enables us to use a very high magnification and still obtain a bright image.

Apochromatic Objectives. These are corrected for chromatic aberration for three colours and generally for spherical aberration for two colours. In practice this means that the images produced by rays of any colour lie in the same plane and are equally sharp. When black-and-white objects are viewed with oblique illumination heavy colour fringes will be obtained with an achromatic objective but only faint ones with an apochromatic; the latter objective therefore enables us to see small coloured objects in their natural colours. With apochromatic objectives attention to correct tube length and cover-glass thickness is of the highest importance.

Resolving Power. When a narrow central pencil of light is used to illuminate the object under the highest magnification, the finest detail which can be seen distinctly is in size equal to $\dfrac{\lambda}{\text{N.A.}}$ where λ is the wave-length of the light used. With a wider pencil this resolving power is increased until it reaches a maximum, when the pencil is just broad enough to fill competely the aperture of the lens; the resolving power is then equal to $\dfrac{\lambda}{2\text{N.A}}$l. The same maximum is obtained with a narrow pencil having the greatest degree of obliquity possible. So with a wave-length of the light equal to 0·00053 mm. and a N.A. of 1 the resolving power has a value of $\dfrac{0 \cdot 00053}{1}$ mm. for a narrow central pencil or 0·000265 mm. for a narrow very oblique pencil or for a cone which fills the aperture.

Depth of focus or penetration is the power of making clear objects which are not in the same plane; this is a very desirable property for chemical purposes. In addition, the penetration is helped by the accommodating power of the eye; the depth obtained in this way is inversely proportional to the square of the magnification. Depth of focus is inversely proportional to the N.A. Increased depth of focus can only be obtained by a loss in efficiency of the objective.

Variable Objectives. These are made so that the distance between the two lens systems can be altered by means of a graduated collar; they are convenient for low-power work.

Selection of Objectives. For the exact study of objects lying in one plane, where brightness of field and high resolving power are the essentials, apochromatic objectives will be used; but for general work of a chemical nature, depth of focus and a long working distance are usually of higher importance than high resolving power, and objectives having these properties will be sought.

Oculars. These are generally negative or Huyghens oculars, in which the real image (1_3, Fig. 25 (VI *)) is formed inside the ocular, as opposed to positive or Ramsden oculars, in which the real image is formed outside; the latter are used in micrometer eyepieces. Oculars are marked either with the number of times they magnify the real image or by the equivalent focus; these quantities are related by the equation

$$\text{Magnification of eyepiece} = \frac{\text{distance of distinct vision}}{\text{equivalent focus}}$$

$$= \frac{(10 \text{ inches or } 250 \text{ mm.})}{\text{equivalent focus}}$$

The total magnification is the product of the magnifications due to the eyepiece and the ocular, but since the marked values are often incorrect —for example, the ocular marked 0·083 inch is usually 0·07143 inch—the actual magnification is given approximately by this calculation.

The point e in Fig. 25 (VI *) is called the eye-point, and is the correct position for the eye in using the microscope; its greatest useful diameter is equal to that of the pupil of the eye, and its least is approximately 1 mm. This diameter is directly proportional to the N.A. of the objective and inversely proportional to the magnification of the ocular. This then gives us the rule for the most satisfactory combination of ocular and eyepiece to obtain a given magnification; namely, for flat objects use a high-power objective and a low-power ocular; this gives a clear image but involves loss of working distance, so that for irregular objects we are compelled to use the combination of a low-powered objective and a higher-powered ocular.

The following table gives some particulars of a series of Bausch and Lomb achromatic objectives :

Equivalent focus		N.A.	Working distance, mm.	Mag. produced by objective alone
mm.	inches			
48	2	0·08	53	2
32	$1\frac{1}{3}$	0·10	38	4
16	$\frac{2}{3}$	0·25	7·0	10
8	$\frac{1}{3}$	0·50	1·6	20
4	$\frac{1}{6}$	0·65	0·6	43
3	$\frac{1}{8}$	0·85	0·2	57
1·9	$\frac{1}{12}$	1·25 (oil)	0·15	95

The table on page 244 gives the magnifications produced by these objectives with Huyghenian oculars and also gives the diameter of the field in millimetres.

Binocular eyepieces have the advantage that they give a true stereoscopic effect and in extended use fatigue is lessened. It is also possible to attach photographic eyepieces so that photomicrographs are easily obtained. A camera with lens removed may also be used provided that light is excluded from outside between the camera and microscope.

Compensating Oculars. With apochromatic objectives, although the different coloured images all lie in the same plane they are not of the same size; therefore with ordinary oculars colour fringes are obtained near the edges of the field; the compensating ocular is designed so as to correct

Objectives	Oculars			
E.F.	5 ×	6·4 ×	7·5 ×	10 ×
48 mm.	10 ×	13 ×	15 ×	20 ×
	10·5 mm.	9·0 mm.	8·5 mm.	8·5 mm.
32	20 ×	26 ×	30 ×	40 ×
	5·5 mm.	4·8 mm.	4·3 mm.	4·4 mm.
16	50 ×	64 ×	75 ×	100 ×
	2·10 mm.	1·85 mm.	1·70 mm.	1·74 mm.
8	100 ×	130 ×	150 ×	200 ×
	1·02 mm.	0·90 mm.	0·83 mm.	0·85 mm.
4	215 ×	275 ×	320 ×	430 ×
	0·48 mm.	0·43 mm.	0·39 mm.	0·40 mm.
3	285 ×	365 ×	420 ×	570 ×
	0·36 mm.	0·32 mm.	0·29 mm.	0·30 mm.
1·9	475 ×	610 ×	720 ×	950 ×
	0·22 mm.	0·19 mm.	0·17 mm.	0·18 mm.

this and give with an apochromatic objective a field which is free from colour right up to the edge.

Parfocal Oculars are designed so that the lower focal planes are all at the same distance from the eye-lens; by this means the eye-pieces can be changed without altering the focus.

In using the microscope the object should first be examined with a low power, and for a final examination the lowest magnification possible should be used. In focusing, the objective should be brought down near to the cover-slip and always be focused upwards. Lenses should be cleaned with lens paper only and particles of dust should be blown off before rubbing with the paper. When the oil immersion lens is used the oil should be wiped off as soon as possible with lens paper, the last traces removed by means of xylene, and the lens then dried and polished with the paper.

Condensers. The object of the condenser is to collect the light and send it through at such an angle that it will fill the aperture of the object-ive. The condenser shown in Fig. 25 (VI *) is an Abbe condenser; it is seen to consist of two lenses and to be provided with an iris diaphragm below; this condenser is not corrected for aberration; it has a N.A. of 1·20 when the diaphragm is full open. When the N.A. of the objective is more than 1·20 a three-lens condenser having a N.A. of 1·40 is used. If the N.A. is greater than 1, a drop of oil must be placed between the con-denser and the bottom of the slide. Aplanatic condensers are used only for photo-micrography and for very high magnifications. The diaphragm controls the amount of light and prevents the field being flooded with too much light; the same result is obtained by lowering the condenser.

Abbe condensers are to be used with a plane mirror whenever possible; a sheet of ground glass can be placed in front of the source of light to pre-vent images formed by the mirror being seen. Accurate centering of the condenser is important; this can be carried out in the following way: Place on a slide a preparation of thin gum which has been beaten up so as to be full of small air bubbles, remove the condenser and bring a very small

air bubble to the centre of the field; focus on this so that it appears as a bright spot surrounded by a dark ring, then tilt the mirror until the bright spot is exactly central in the dark ring; the light from the mirror is now axial. Replace the condenser and raise it about half-way. If the condenser is central, on raising and lowering the body tube by means of the coarse adjustment there will be no alteration in the position of the bright spot or movement of the image. If necessary adjustment is made by means of the two centering screws.

Below the condenser generally is fitted a ring which swings in or out: when using artificial yellow light a slip of blue glass is placed in the ring to cut out the excess of yellow light. If a disc of metal with an eccentric circular hole is placed in the ring, oblique light passes out of the condenser, and this is convenient for differentiating between the upper and lower surfaces of a thin transparent object.

Dark Ground Illumination can be obtained by using a central dark stop below the Abbe condenser with the diaphragm fully open, a drop of water being placed between the top of the condenser and the bottom of the slide; or by the use of special condensers such as the Bausch and Lomb (see Paraboloid Condenser, Chapter V *, S.1, Colloids) or the Leitz (Fig. 26 (VI *)); it will be seen that these bring the oblique light to a focus at a point just below the cover-slip, so that slides of the correct thickness must be used. A powerful source of light is necessary and objectives of N.A. not greater than 1 are used. Very small objects can then be studied and will appear as bright self-luminous bodies against a black background. Ultra-condensers are designed to give still more oblique light, enabling the
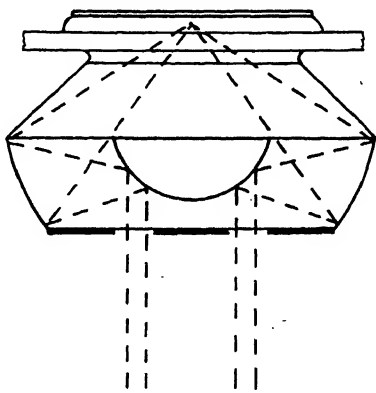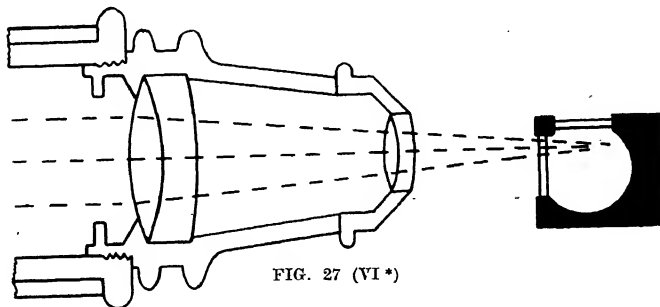
FIG. 26 (VI *)

FIG. 27 (VI *)

presence of still smaller particles to be demonstrated, but always with less resolving power, until in the ultra-microscope (Fig. 27 (VI *)), where a lateral beam of light is used, the objects appear as diffraction discs in which the appearance of the object is lost entirely.

Illumination by Reflected Light is used in the examination of the surface of objects. Oblique light may be reflected down on to the object
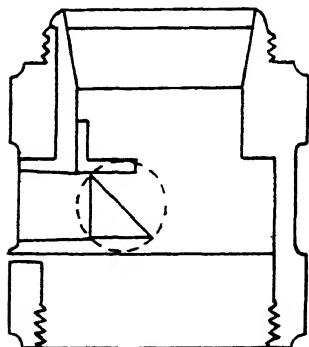

FIG. 28 (VI *)

by means of a small mirror attached to the objective or by placing a source of light at a higher level and concentrating it on to the object by means of a lens. A device for obtaining axial reflected light is shown in Fig. 28 (VI *); this is an adapter which screws into the lower end of the body of the microscope and is threaded for the insertion of the objective. In the example shown the reflecting device is a 45° prism mounted to one side of the axis; arrangements are sometimes provided for turning the prism, and an iris diaphragm is used to cut down the light. In other forms a disc of glass or mica with its plane inclined at 45° to the vertical is mounted on a horizontal axis passing through the optic axis of the microscope.

A type of microscope made for chemical purposes by Bausch and Lomb is shown in Fig. 29 (VI *). The instrument is fitted with a coarse and a fine adjustment; if the latter, A, has a micrometer screw and is graduated, it can be used in the measurement of the thickness of small objects and for determinations of refractive index by the 'apparent depth' method.

The stage is circular and revolving; it has a milled edge and is graduated in degrees; the top is of vulcanite and is provided with spring clips C and centring screws D. It can be removed by unscrewing the centring screws and then lifting it out bodily, thus enabling an auxiliary stage to be inserted in the substage ring: this auxiliary stage can then be moved up or down by means of the rack and pinion of the substage. This is a great convenience in the examination of thick objects or of opaque objects by means of vertical illumination. The substage consists of a simple ring which is adjustable by means of a quick-acting

FIG. 29 (VI *)

screw of long range; when the screw is moved right down the ring can swing out to the side. The condenser, polarizer and auxiliary stage are all made to fit in the same ring. The polarizer E is a Nicol prism mounted with a revolving ring graduated at intervals of 2° and fitted
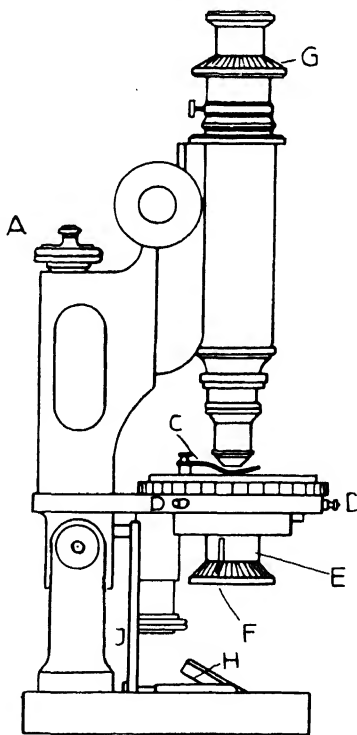
with a pointer F. The mounting fits into the ring on the substage and is held in position by a stud fitting into a slot. The analyser G consists of a Thompson prism also mounted with a revolving ring graduated in 2° divisions : the collar moves in a cylindrical mounting fitted over a draw-tube ; it is slotted so as to engage a stud and so fix the zero-point. The draw-tube is mounted so that it can only move vertically ; thus, when the analyser and polarizer are both set to the zero reading they are in the crossed position and no time need be spent upon adjustment.

The mirror H is a large one and is plane on one side and concave on the other ; it is fitted to an arm J which can swing out to the side and by means of auxiliary arms the mirror can be brought up to such a position that it will act as a vertical illuminator. Objectives of long working distance and of E.F. 32, 16, and 8 mm. and oculars 5 ×, 7·5 ×, 10 ×, and 12·5 × are suitable, and of these one high-power and one low-power should be provided with cross-hairs. This equipment gives a range of magnification of from 20 to 260 diameters.

Camera Lucida. This useful adjunct to the microscope is shown in Fig. 30 (VI *). It fits over the eyepiece and is fastened by means of a clamp-ring. It consists of a glass cube B cut diagonally ; one of the diagonal faces is silvered except for a small circle at its centre, and the two halves are cemented together again. A sheet of paper placed on the bench at the side of the microscope is seen by an eye placed at e by reflection first at the mirror surface M, and then at the silvered surface S ; the eye also sees the image formed by the microscope through the small unsilvered
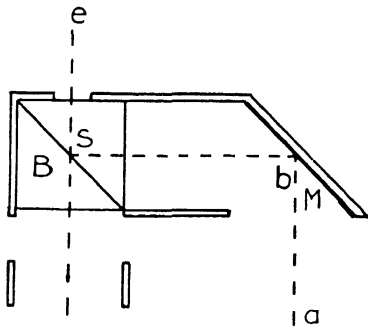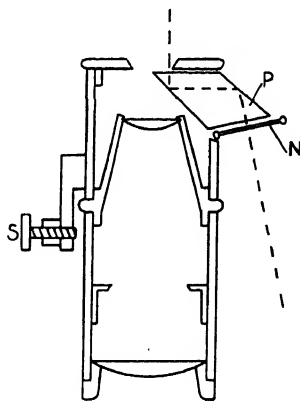
FIG. 30 (VI *)   FIG. 31 (VI *)

circle. If a pencil is placed on the paper the image of its point may be made to coincide with a point on the image of the object under the microscope, and the outline of this image can then be followed by the pencil point, so obtaining a drawing of the image. To prevent distortion the line ab must be at right angles to the paper on which the drawing is made. Neutral-tinted glasses can be slipped into a clip so as to reduce the intensity of the light reflected from the paper. The drawing eyepiece shown in Fig. 31 (VI *) is used for the same purpose. The rays from the sheet of paper are totally reflected twice in the prism P. Here also neutral-tinted

glass can be inserted at N. The screw S fixes the eyepiece firmly to the draw-tube.

Either of these devices can be used in micrometry, i.e. to measure the size of an object. To do this first the object is placed on the stage and is focused and drawn on the sheet of paper. The object is removed without displacing any of the rest of the apparatus and in its place is put a stage micrometer on which is ruled a millimetre subdivided into 100 parts ; the micrometer is moved until its image appears to cross or lie very near to the drawing on the paper, and a drawing of the scale is then made over the part of the object to be measured. The number of divisions covered by the object can be estimated, and since each division is 0·01 mm. the size of the object can be ascertained.

A Micrometer Eyepiece. Such an eyepiece with a fixed scale can also be used in combination with a stage micrometer. The microscope is
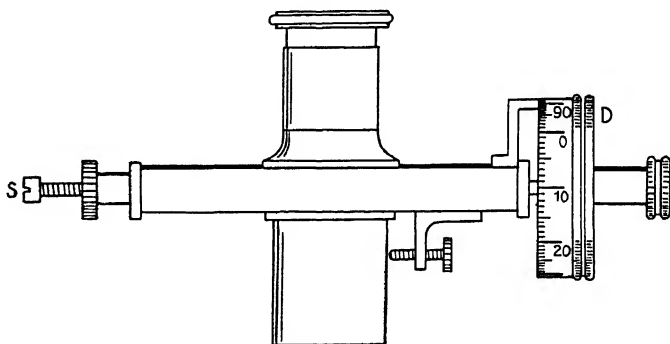
FIG. 32 (VI *)

focused on the latter and in general the divisions will be found not to coincide ; the stage micrometer is moved so as to get coincidence with the middle division of the fixed scale and the length of the draw-tube is altered until the remaining divisions of the two scales also coincide exactly ; when this result has been obtained, the value of the fixed-scale division is equal to the length of the stage-scale division, and if without altering the length of the draw-tube the stage scale is replaced by the object to be measured, the image of this will cover a number of fixed-scale divisions of known magnitude.
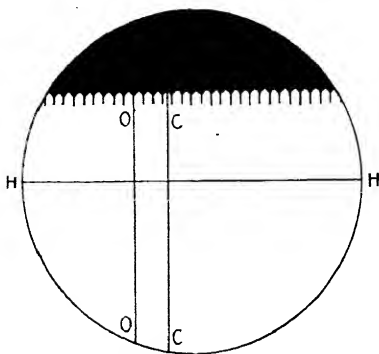
The filar micrometer eyepiece shown in Fig. 32 (VI *) has the advantage that no estimate has to be made of fractions of a division. Fig. 33 (VI *)

FIG. 33 (VI *)

shows the appearance seen on looking into the eyepiece ; the black comb, the zero line O and the horizontal line HH are all connected together, and can be moved as a whole across the field by means of the screw S. The line

C is moved by the drum D so that one complete rotation of the drum moves the line exactly one division of the comb. The drum is divided into 100 parts so that 0·01 of a scale division can be read off. The use of the instrument will be apparent from a description of a method of finding the value of a scale division. The stage micrometer is placed so that its divisions are parallel to those of the eyepiece. The screw S is turned until the line O coincides with a division on the stage scale. The drum D is turned until the line C coincides with the tenth scale division, and its reading is again taken; the number of complete turns of the drum is obtained from the number of teeth on the comb and the fractions of a tooth from the difference of the two drum readings; thus in the diagram the number of complete turns of the drum is three and the difference in the drum readings will be about fifty. Such devices are of special value in connexion with the ultra-microscope (see Chapter V *, S. 1).

Hot Stages. A simple hot stage suitable for the determination of the melting-points of substances which melt below 100° is shown in Fig. 34 (VI *). It consists of a parallel-sided glass cell fitted with a rubber stopper carrying an inlet tube, an outlet tube, and an Anschutz thermometer. The sub-
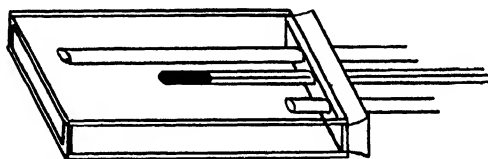
FIG. 34 (VI *)

stance to be examined is placed on the cell and is brought into focus; if a camera lucida is available this may be arranged to view the thermometer at the same time as the object. Hot water is circulated through the cell from a heater such as that used with the Abbe refractometer. A hot stage for higher temperatures is shown in Fig. 35 (VI *). This consists of a disc
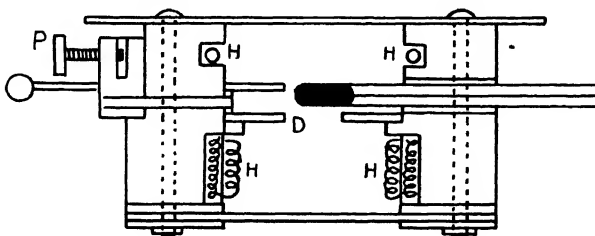
FIG. 35 (VI *)

of alberene stone closed by a mica window at the bottom and by a glass slide at the top; it is heated by passing a current through the resistance wires shown at HH, the temperature being regulated by means of a rheostat. D is a removable metal disc which cuts down the opening in the stage and also acts as a radiator. P is one of the binding posts, and C is one of the sliding pins which serve to support small crucibles and so on in the chamber. An Anschutz thermometer is shown at T.

The Polarizing Microscope. This microscope is extremely useful for examining crystals. In using it the first point to be tested is whether the nicols are properly crossed when their mountings are fitted so that the studs fall into the slots and the pointers are both turned to zero. The analyser and objective are removed and the plane mirror is set so as to obtain the brightest possible field. The analyser is replaced and both scales set to zero. The space between the objective and the aperture in the stage is screened with a black cloth so as to prevent the entrance of extraneous light, and with the head under a black cloth, such as is used by photographers, the appearance is examined to see if the maximum extinction has been obtained ; this is done by turning one of the nicols slightly in each direction to see if more light passes through. Several settings are made and readings noted. The stage is next centred by placing a slide thereon and using a low-power objective ; a small speck on the surface of the slide is focused and the slide moved with the fingers until this spot lies under the intersection of the cross-hairs. The stage is then rotated, and if it is centred correctly the spot will remain under the cross-hairs : if not, the spot will move in a circle. Note the position of the centre of this circle and by means of the centring screws bring this point under the cross-wires ; then move the slide so as to get the mark on its surface under the centre of the cross-wires ; by repeating this two or three times the stage can be centred accurately. The cross-hairs of the eyepiece should correspond with the planes of vibration of the Nicol prisms. To test this, place a drop of mercuric chloride solution on a slide and allow it to evaporate slowly and so get a crop of small crystals ; with the nicols crossed correctly select a flat crystal with a long edge, and move the slide so that this edge lies along a cross-wire near the centre of the field. Now on turning the stage circle the maximum extinction should be obtained each time the edge of the crystal becomes parallel to a cross-wire. Mercuric chloride is a substance exhibiting what is called parallel extinction ; some other crystals, e.g. copper sulphate, exhibit oblique extinction, i.e. the maximum darkness is obtained when the edge of the crystal is inclined to the cross-hairs.

When a crystal is placed on the stage between the crossed nicols and the stage is rotated the crystal may undergo no change in appearance ; in that case it is isotropic and belongs to the cubic system. Alternatively it may show extinction which may be parallel or oblique : in this case it is anisotropic or doubly refracting. Doubly refracting crystals fall into two classes : uniaxial crystals are those in which there is one direction through the crystal which is not doubly refracting ; biaxial crystals have two such directions. Uniaxial crystals belong to the tetragonal or hexagonal systems, while biaxial crystals are either rhombic, monoclinic, or triclinic.

If, with nicols crossed, a uniaxial crystal is placed so that its optic axis is parallel to a cross-hair, no change will be observed on rotating the stage, but for every other position of the crystal extinction will be observed ; the optic axis can thus be found experimentally. To determine whether extinction is parallel or oblique a crystal is turned until extinction is obtained and the scale reading is noted ; the analyser is then removed and the stage is turned until the edge or a cleavage plane is parallel to a cross-hair and the angle of rotation of the table is read ; this angle will be 0°

or 90° in the case of parallel extinction, and if a number of crystals give this result the system must be tetragonal, hexagonal, or rhombic ; if not it must be either monoclinic or triclinic (see Chapter on Crystals).

Selenite Plate. When the double refraction of a substance is very weak, the change in appearance when it is rotated between crossed nicols is not pronounced. A selenite plate is cut to such a thickness that when placed with its vibration plane at 45° to the plane of the nicols, a purple-red coloured field is produced. With this plate a weak double refracting substance will appear of a contrasting colour, so that the presence of the weak double refraction can be detected ; the actual colours observed depend on the thickness of the crystals. The plate is marked with two dots so that it can be placed over the eyepiece with the line joining the two dots bisecting the angle between the cross-wires. In using it to measure extinction angles the crystal is brought so that its long edge lies parallel to a cross-wire and the reading on the circle is taken ; the circle is then turned until the crystal is of the same colour as the field and the angle read through which it has been turned : if the crystal belongs to the monoclinic or triclinic systems it will yield two extinction angles ; the smaller is the one recorded. The observation should be repeated on a number of crystals.

Cross Wires in Microscopes. A description of the practical technique in fixing or replacing cross wires in optical instruments is given by Ansley.[1] The use of ' glue ' for the production of cross wires is described by Drummond.[2] He obtained fibres of different diameters by the use of varying types of ' glue '. Silkworm cocoon gave threads of 0·01–0·02 mm. diameter. Seccotine gave 0·002–0·004 mm. diameter and Certofix[3] gave 0·001 mm.

[1] *Introduction to Laboratory Technique*, MacMillan, 1938.
[2] *J. Sci. Inst.*, 1933, *10*, 259.
[3] Made by the British Isinglass Co., Grimsby.

SECTION 5: COLORIMETRY AND NEPHELOMETRY

Introduction. Quantitative measurements based on the colour of solutions have been long used, perhaps the best known being the determination of ammonia by Nessler's solutions. Of more recent date are similar measurements based on the amount of light reflected by a cloud of finely divided precipitate, as, for example, used by Richards to determine small amounts of chloride by means of the cloud of silver chloride produced by the addition of silver nitrate to an extremely dilute chloride solution.

Nessler Tubes. The simplest form of apparatus for colour measurements consists of the Nessler tubes, shown in Fig. 36 (VI *). The tubes have parallel sides and flat bottoms and have a graduation mark at 50 and 100 ml. The tubes should be of the same diameter, but frequently are not. They should therefore be tested for equality of distance between the 50 and 100 ml. marks and a selection made of those which agree. As an example of their use may be taken the estimation of dilute solutions of ammonia in water; 50 ml. of the water to be tested are placed in one glass. A standard solution of ammonium chloride, containing 3·15 grams of ammonium chloride per litre, is prepared, using ammonia-free water. This is diluted 100 times before use, and then contains 1 part of ammonia in 100,000. Solutions are prepared by taking 1, 2, 3, &c., ml. of the ammonium chloride solution, placing in Nessler tubes and adding ammonia-free water up to the 50 ml. mark. These comparison solutions now contain 0·02, 0·04, 0·06, &c., parts of ammonia per 100,000. 2 ml. of Nessler solution are then added to each of the test and comparison solutions, and, after mixing, the glasses are placed on the stand, where they rest on a piece of transparent glass, below which is a sheet of white opal glass. On looking
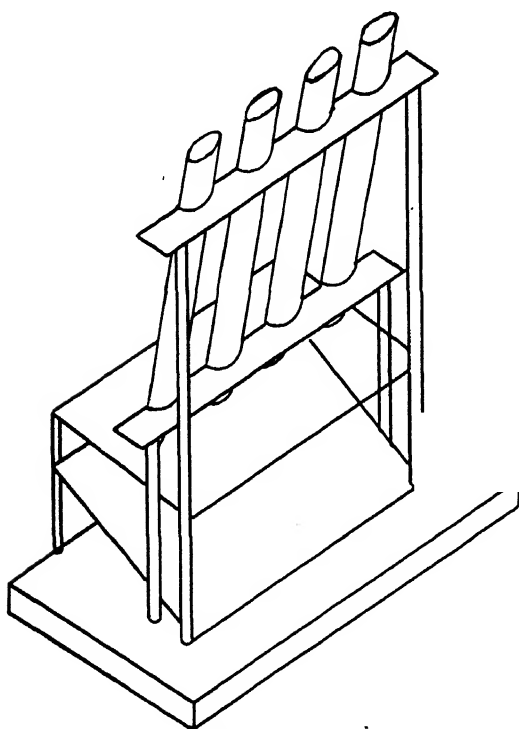
FIG. 36 (VI *)

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vertically down through the solutions, the variations in the brown tint are apparent, and the colour of the test solution can be matched against one of the comparison solutions, or can be placed between two of the comparison solutions, enabling the ammonia to be estimated to 0·01 parts per 100,000.

The Duboscq Colorimeter is shown in Figs. 37 (VI *) and 38 (VI *), the optical arrangement being included on the right-hand side of the figure. Light is reflected from the mirror M at the base up through the liquids in
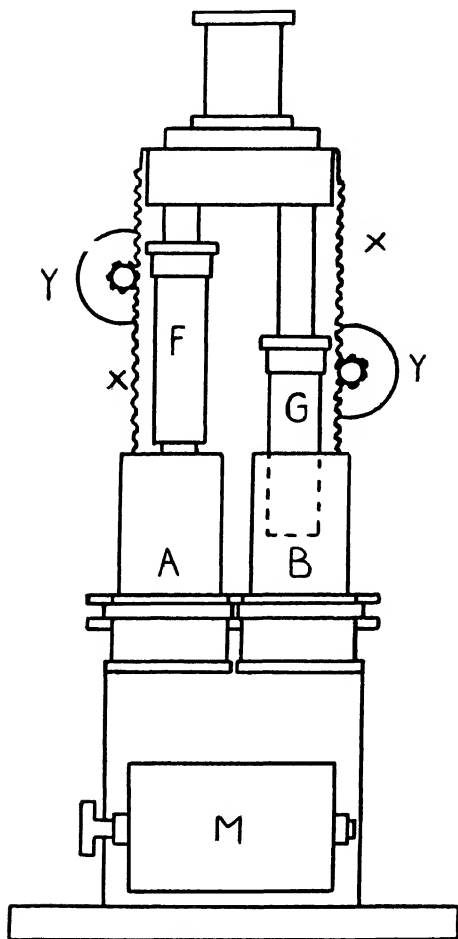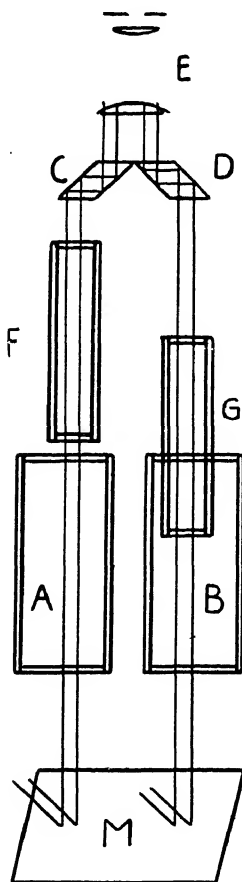
FIG. 37 (VI *)   FIG. 38 (VI *)

the comparison tubes A and B, into the prisms C and D which reflect the light twice and bring the two beams side by side in the eyepiece E, as shown by the ray lines. The cups A and B are removable for cleaning. The tubes F and G are closed at both ends and in recent forms consist of solid rod. They are movable in a vertical direction by means of the milled heads Y to which are attached pinions engaging with the racks X. Attached to F and G are verniers moving over scales graduated from 0–6 cm. on the

back of the stand. A blackened metal figure, not shown in the diagram, surrounds the cups and prevents the entrance of lateral light. To make a measurement the instrument is placed facing a northern light if possible; if opposite a window a piece of tissue paper, fastened to the glass by means of gum at the four corners, serves to diffuse the light. The mirror at the base is turned so as to reflect light up through the instrument, and the latter is moved until the two halves of the field appear to be equally bright. It is best to test this by filling both the cells A and B with the comparison liquid and trying whether equal depths of liquid produce equal brightness in the two halves of the field. To make a measurement the standard coloured liquid is placed in A and the liquid to be measured in B. The tubes F and G are lowered until their ends dip into the liquid, taking care that air bubbles are not included under the ends of the tubes. On looking through the eyepiece the two halves of the field will appear unequally coloured. Suppose that the colour due to B appears to be deeper than that due to A. Lower the tube G by means of the thumb-screw until the colour appears to be the same on both sides, and read the two verniers. Now lower G a little and then raise it until the colour matches again; read the vernier on G. Repeat this several times, approaching the match from either side by means of G, and take the mean of all these readings. Now determine the zeros by lowering the tubes F and G until they touch the bottoms of A and B. Suppose the following readings were obtained:

$$\begin{aligned}
\text{Vernier readings of F} &= 4 \cdot 52 \text{ cm.}\\
\text{Zero reading of F} &= 0 \cdot 02 \text{ cm.}\\
\text{Then depth of liquid in A} &= 4 \cdot 50 \text{ cm.}\\
\text{Mean of vernier readings of G} &= 3 \cdot 23 \text{ cm.}\\
\text{Zero of vernier readings of G} &= 0 \cdot 00 \text{ cm.}\\
\text{Then depth of liquid in B} &= 3 \cdot 23 \text{ cm.}
\end{aligned}$$

$$\frac{\text{Colour of liquid in B}}{\text{Colour of standard in A}} = \frac{\text{Depth of A}}{\text{Depth of B}} = \frac{4 \cdot 50}{3 \cdot 23} = 1 \cdot 393$$

Improved Procedure. A method of procedure which eliminates to some extent the difficulty of obtaining equality of illumination in the two sides of the instrument consists in placing standard solution in both A and B and finding the mean reading of B which corresponds to a fixed reading of A. The standard liquid in B is then replaced by the test liquid, and the mean reading of this which corresponds to the same fixed reading of A is determined.

For cleaning, F and G are raised and A and B can then be removed laterally. The glass bottoms of A and B are removable by turning the metal base pieces.

The disadvantage of the Duboscq instrument is that it is very difficult to secure equality in the two fields. Folin and Denis [1] suggest that this is due to the ageing of the Canada balsam used in sealing the glass plate above the prisms, and they recommend the removal of this plate with xylene. These writers also point out that the eye is far less sensitive to variations in light when one has just looked at the bright sky or bright objects out-of-doors. They recommend placing the colorimeter near the centre of the

[1] *J. Biol. Chem.*, 1924, **36**, 485.

room on a low stool and sitting on a chair at the side, rather than behind, to take the readings. Colour-matching is very tiring to the eye, and fatigue is fatal to good colorimetric work, so that for a long series of readings attention should be paid to details which will reduce eye fatigue as much as possible. It is very noticeable that with practice one's capacity for matching colours improves rapidly. The Duboscq cups are only 5 cm. deep, so that when the variations in the amount of colour are great, there is considerable loss of accuracy. The cups have cemented bottoms so that they cannot be used for all solvents.

A Klett modification of the above instrument was used by Reilly and Bastible [1] to estimate nitrous acid colorimetrically. The solutions were placed in cups, with fused bottoms, free from optical defects. Dipping into these cups are fixed plungers, which, like the cups, have opaque walls and transparent bottoms. The cups are carried on stages which are movable. 2 mm. scales, with verniers attached, are used to measure the heights of the liquid columns, which decrease as the cups are moved upwards. When the cups are screwed up so that they make contact with the bottom of the plunger, the verniers should both read zero. These verniers are movable, and so are capable of adjustment.

Diffused daylight is reflected up by mirrors through the two solutions to the top of the plungers. These reflectors work independently of each other, and the reflected light can be adjusted so as to ensure a very even field. The rays from the two sides are brought to a common field by means of an observing microscope, which also allows the fine dividing line to be sharply focused. The depth of the standard solution is set at a convenient mark, the depth of the other being varied by means of the coarse and fine adjustments until the two halves of the field are identical in appearance. A reflecting mirror at the top allows the scales to be read from the same point of observation as the colour fields.

The necessary calculations are simple. The assumption is that the depth of colour is proportional to the concentration of the substance. The depths of the solutions, therefore, vary inversely as the concentrations in the standard and in the unknown respectively. If the standard contains a certain amount of material in a given volume, and the unknown is made up to the same volume, then from the readings of the standard and the unknown the amount in the latter can be calculated.

Kober's Colorimeter. Kober [2] describes a colorimeter in which most of the objections are removed. The optical system is shown in Fig. 39 (VI *). B represents one of the plungers with sides of black glass and ends F of optical glass fused on instead of cemented. C shows the prism arrangement which gives the Lummer-Brodhun field, as shown at E, where the square in the centre is coloured by the liquid on the right and the surrounding part by the liquid on the left. The instrument is shown in Fig. 40 (VI *). The plungers are fixed to the head so that no dust can collect above them. The verniers are adjustable so that an accurate zero-point can be obtained. Heights up to 11 cm. can be measured; the cups have black glass slides and transparent glass bases fused on. The screw attachments for raising

[1] *Sci. Proc. Roy. Dub. Soc.*, 1926, **18**, 28, 343.
[2] *J. Biol. Chem.*, 1917, **29**, 155.

the cups have a small milled head T and a large one R, these giving a quick and slow motion (Fig. 41 (VI *)).   The remaining point is to secure equality of illumination of the two fields ; this is done by means of the lamp and lamp-house shown in Fig. 41 (VI *).   The lamp is a concentrated tungsten-
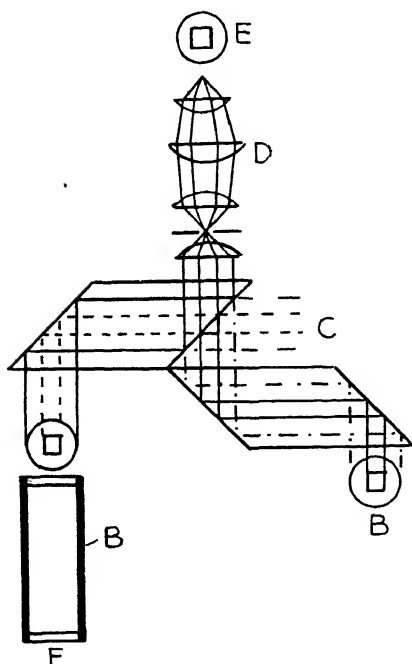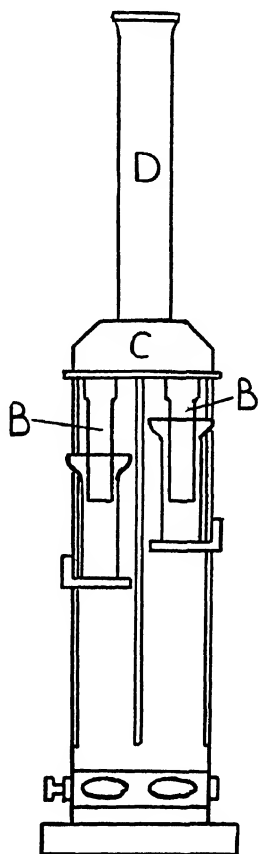
FIG. 39 (VI *)   FIG. 40 (VI *)

filament lamp (110 volt), and the light passes through a sheet of glass B to reduce heating, and then through the condenser C (lettering on left of diagram).   The reflectors A are made in pairs, so that the light which falls on each side of the colorimeter can be separately adjusted so as to produce equality of the field.

Determination of the Solubility of Silver Chloride in Water and the Solubility Product.   This method is due to Whitby,[1] and depends upon the fact that dilute silver solutions with cane sugar and caustic soda give a yellowish brown silver solution which is adapted for colorimetric measurements.

For comparison a standard silver nitrate solution is required.   Dissolve 0·170 gram of silver nitrate in 1 litre of water, thus obtaining a 10^{-3}N.

[1] *Zeitsch. anorg. Chem.*, 1910, 62.
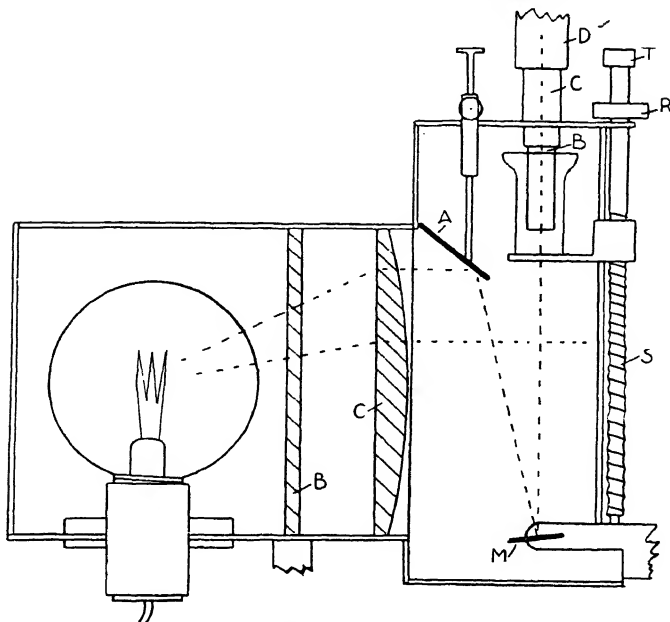
FIG. 41 (VI *)

solution. Dilute 10 ml. of this to 1 litre to get the 10^{-5}N. solution of silver nitrate which will serve as the standard.

Precipitate some boiling silver nitrate solution with potassium chloride solution. Allow this to stand until the precipitate has settled down and pour off the mother liquid, pressing the precipitate with a glass spatula. Wash the precipitate very thoroughly with seven changes of distilled water and transfer half of it to each of two 250-ml. bottles.

Prepare a 10^{-5}N. solution of potassium chloride. Dissolve 0·746 gram in one litre, dilute 10 ml. of this to 100 ml. and 10 ml. of the last solution to 1 litre ; be careful to wash the pipette thoroughly each time.

To one of the bottles containing the silver chloride add 200 ml. of the potassium chloride solution, shake thoroughly and after the silver chloride has settled pour off the mother liquor as completely as possible. Repeat the washing with a second portion of the potassium chloride solution and then add 200 ml. and replace the stopper. Treat the silver chloride in the second bottle in a similar way, using distilled water instead of the potassium chloride solution. Keep the bottles in a cupboard until next day, shaking them vigorously as often as may be convenient.

On the following day take three 100-ml. flasks and add 50 ml. of the standard silver nitrate to the first, 50 ml. of the aqueous solution of silver chloride to the second and 50 ml. of the potassium chloride solution of silver chloride to the third. To each flask add 10 drops of a concentrated solution of sucrose and heat in a beaker of boiling water for 2 minutes ; then to each add 6 drops of N. sodium hydroxide and replace in the boiling water for 30 seconds ; cool under the tap and the solutions are ready for the colorimetric measurement.

Place the standard silver nitrate solution in A and the aqueous silver chloride solution in B. Lower the tubes F. and G until their ends dip into the liquid, taking care that air bubbles are not included under the ends of the tubes. On looking through the eyepiece the two halves of the field will appear unequally coloured. Suppose that the colour due to B appears to be deeper than that due to A. Lower the tube G by means of the thumb-screw until the colour appears to be the same on both sides, and read the two verniers. Now lower G a little and then raise it until the colour matches again; read the vernier on G. Repeat this several times, approaching the match from either side by means of G, and take the mean of all these readings. Now determine the zeros by lowering the tubes F and G until they touch the bottoms of A and B. Suppose the following readings were obtained :

Vernier reading of F . . . . . . = 4·52 cm.
Zero reading of F . . . . . . = 0·02 cm.
Then depth of liquid in A . . . . . = 4·50 cm.
Mean of vernier readings of G . . . . = 3·23 cm.
Zero reading of G . . . . . . = 0·00 cm.
Then depth of liquid in B . . . . . = 3·23 cm.

$$\frac{\text{Colour of liquid in B}}{\text{Colour of standard in A}} = \frac{\text{Depth of A}}{\text{Depth of B}} = \frac{4\cdot50}{3\cdot23} = 1\cdot393$$

Since the standard is 10^{-5}N. the aqueous silver chloride solution is $1\cdot393 \times 10^{-5}$N. and contains $1\cdot393 \times 10^{-5} \times 143\cdot5 = 0\cdot00200$ gram of silver chloride per litre.

If the silver chloride is completely dissociated, the concentration of each ion is $1\cdot393 \times 10^{-5}$ gram ions per litre, and the product of the concentrations of the ions, i.e. the solubility product, is

$$1\cdot393 \times 10^{-5} \times 1\cdot393 \times 10^{-5} = 1\cdot94 \times 10^{-10}.$$

In the same way measure the colour of the solution of silver chloride in 10^{-5}N. KCl. Suppose that this turned out to be 0·96 that of the standard; then the concentration of silver is $0\cdot96 \times 10^{-5}$N.; the concentration of chloride ion is the sum of $0\cdot96 \times 10^{-5}$ from the silver chloride and 1×10^{-5} from the potassium chloride, i.e. the chloride ion concentration is $1\cdot96 \times 10^{-5}$.

The solubility product

$$= C_{Ag^+} \times C_{Cl^-} = 0\cdot96 \times 10^{-5} \times 1\cdot96 \times 10^{-5}$$
$$= 1\cdot88 \times 10^{-10}$$

Estimation of the Dissociation Constant of a Weak Acid (or Base) by the Colorimetric Method.—When the weak acid AB is dissolved in water it is partially dissociated into its ions,

$$AB \rightleftharpoons A + B \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If the fraction which is dissociated is denoted by α, then $1 - \alpha$ is the amount of undissociated acid; and if 1 gram equivalent is dissolved in v litres, the concentration of the undissociated acid is $(1 - \alpha)/v$ and that of each ion α/v.

Applying the law of mass action to equation (1)

$$K_c = \frac{\alpha^2}{(1 - \alpha)v} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This is the well-known Ostwald's Dilution Formula and K_c is the equilibrium constant. In this case K_c is called the dissociation constant of the acid and its numerical value is a measure of the strength of the acid. A similar line of reasoning applies to the dissociation constant of a weak base.

Method.—The colour of the so-called indicators in dilute solution depends mainly on the hydrogen or hydroxyl ion concentration of the solution. In the case of a strong acid in dilute solution we may assume complete dissociation without great error. So that by dilution of a strong acid of known normality we can obtain solutions of known H^+ ion concentration of any desired value. The colours given by these solutions with a suitable indicator can then be compared with that given by the indicator with solutions of the weak acid of known acid concentration (but unknown H^+ ion concentration) and when a match is obtained the H^+ ion concentration of the two solutions will be the same; since that of the strong acid is known we have obtained that of the weak acid, and knowing the total concentration of this we can now calculate the concentration of the undissociated portion and so work out the dissociation constant from equation (2).

Verification of the Law of Mass Action and determination of the Dissociation Constant of Acetic Acid at Room Temperature. Prepare decinormal solutions of hydrochloric and acetic acids and determine their concentrations by titration against caustic soda, using phenolphthalein as indicators.

Dilute the hydrochloric acid 100 times so as to obtain 0·001N. HCl. Dilute the acetic acid to obtain 0·020, 0·015, 0·010 and 0·005N. solutions. Using Nessler tubes, take 10 ml. of each of the acetic acid solutions and add to them three drops of a dilute methyl orange solution. By means of two 10-ml. burettes, one containing the 0·001N. HCl and the other distilled water, prepare five tubes, containing respectively, 7, 6, 5, 4, and 3 ml. of the hydrochloric acid and 3, 4, 5, 6, and 7 ml. of water and to each tube add three drops of methyl orange. The H^+ ion concentrations of these solutions will be 0·0007, 0·0006, &c.

Now with the aid of the simple colorimeter shown on p. 252 it will be possible to find the limits of H^+ ion concentration between which each of the acetic acid solutions lies; for example, in the case of the 0·01N. acetic acid: the 0·0004N. HCl might be found to be more yellow and the 0·0005N. HCl more red and it might be judged that the acetic acid colour was nearer to that of the 0·0004N. HCl. A series of tubes would then have to be prepared containing 4·1, 4·2, 4·3 and 4·4 ml. of 0·001N. HCl and 5·9, 5·8, &c., ml. of water and three drops of methyl orange, and the comparison again made. If the acetic acid were now found to have a colour between that of the 0·00042N. HCl and the 0·00043N. HCl, its hydrogen ion concentration might be taken to be 0·000425N.

Now if the exact concentration of the acetic acid were 0·01025N., that of the undissociated portion would be 0·01025 − 0·000425, and

$$K_c = \frac{(0 \cdot 000425)^2}{(0 \cdot 01025 - 0 \cdot 000425)} = 1 \cdot 84 \times 10^{-5}$$

The hydrogen ion concentration of each of the other acetic acid solutions is to be found in exactly the same way and the results obtained used

to work out the dissociation constant. If the four values obtained for K_c agree, the mass action law is proved and the mean of the values obtained is returned as the dissociation constant of acetic acid at the temperature of the experiment.

Walpole's Colorimeter. A simple colorimeter which is useful in the titration of coloured solutions is due to Walpole. It consists of a wooden case with a hinged front, and has an inclined sheet of opal glass at the base to reflect light upwards. The case contains two pairs of tubes, A and B above and C and D below, so that light passes through C and A or D and B. As an example of the use of the apparatus 10 ml. of the coloured liquid are placed in the upper cups A and B, equal amounts of indicator are placed in B and C, and in C is placed 10 ml. of a mixture of the standard reaction to which it is desired to titrate, 10 ml. of water being placed in D. To the tube B standard acid or alkali is added until, on looking down the tubes, the colours match. Some solutions exhibit dichromatism and so may show different colours according to the thickness of the layer viewed. For example, solutions of brom-phenol blue appear blue in thin layers and red in thick ones. The absorption bands lie mainly in the yellow and green, so that red and blue are the chief colours transmitted.

If I is the intensity of the light, a the transmission coefficient, and x the thickness of the layer, the intensity of the transmitted light is Ia^x.

Suppose the initial intensities are :

$$\text{Blue} = 100, \quad \text{red} = 30, \text{ and } a_b = 0\cdot5, \ a_r = 0\cdot8.$$
If $x = 1$, $1_b a_b{}^x = 50$, $1_r a_r{}^x = 24$ ml. blue is greater than red.
If $x = 10$, $1_b a_b{}^x = 0\cdot10$, $1_r a_r{}^x = 3\cdot0$ ml. red is greater than blue.

This illustrates the necessity for trying whether a correct comparison can be made with solutions of different strengths. A colorimetric curve should be drawn by comparing solutions of gradually increasing strength against a standard solution and plotting the ratio of the strengths against the colorimeter reading. The theoretical curve can readily be calculated. E.g. suppose with equal strengths of the standard the colorimeter reading is taken as 10 ; then, if a solution of twice the strength is used, the colorimeter reading should be 5, while if one of one-third the strength is used it should be 30. In practice this will frequently be found not to be the case, and the experimental curve should then be used to calculate the relative strengths. Similarly with nephelometer readings. In the Bernoulli colorimeter the instrument is set horizontal and has a sliding scale. Tests can be made with as little as 0·1 ml.

Spekker Photoelectric Absorptiometer. The visual method of making colour comparisons with instruments of the Duboscq type is fatiguing to the eye and is not very accurate : in addition one often finds a change in the tint of a solution on dilution so that it is extremely difficult to match a long column of the dilute solution against a shorter one or a more concentrated one of the same substance. These difficulties are overcome in the absorptiometer in which not the depth of colour but the total absorption of light is measured and the eye is replaced by a pair of photoelectric cells. When a single photoelectric cell is used great care has to be exercised to avoid voltage fluctuations in the current supply to the lamp, involving

running this from batteries. Again, with a single cell certain assumptions have to be made regarding the intensity-current characteristic of the photo cell used and this may change with age of the cell.

In the Spekker instrument which is made by Hilgers these difficulties are overcome by using a pair of photo cells in opposition so that when a reading is taken the voltage drop across the cells is zero, which is indicated by a galvanometer showing no deflection when balance is reached, and a linear relationship is always maintained between the current and the intensity.

A plan of the optical arrangements and the electric circuit is shown in Fig. 42 (VI *). A is a 100-watt projector lamp housed in a cylindrical lamphouse and run from the electric mains supply : this serves as the source of light. The lens B on the right of the lamp forms a parallel beam of light which passes through the specimen S to the lens C which forms an image of the filament of the lamp on the photo cell D (the indicating cell). E is a calibrated variable aperture between the lamp and the lens system : by this means the intensity of the light falling on the photo cell can be varied by known amounts, and since an image of the filament is formed on the photo cell there is no change in the cell area which is illuminated when the aperture E is altered. The scale attached to E is so calibrated, that if R is the scale reading when the aperture is opened, so that the amount of light transmitted is $1/a$ of that
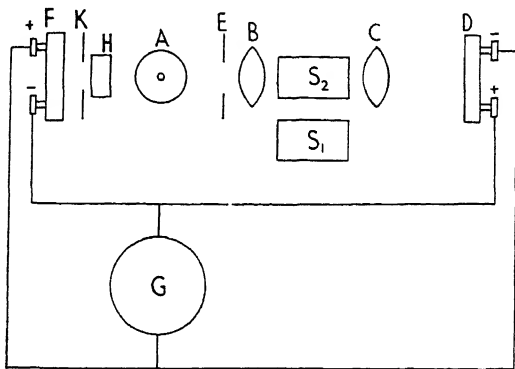

FIG. 42 (VI *)

transmitted when the aperture is fully open, then $R = \log a$: this function is approximately linear with the concentration of the solution over small ranges. Light from the source A after passing through a 1-cm. water cell H also falls on the photo cell F (compensating cell) on the left. The amount of light falling on this cell can be varied by means of the iris diaphragm K, which is provided with a fine adjustment. The two photo cells D and F are connected in opposition across the galvanometer as shown.

The photoelectric cells used are of the 'rectifier' type which do not need external batteries.

The solutions to be compared are contained in the two cells S_1 and S_2 (1 cm. or 4 cm. long, the smaller cell taking 7 ml. of liquid) ; the cells are mounted side by side on a slide which can be pushed across so as to put either in the beam.

In taking a reading the more absorbing liquid S_2 is first placed in the beam and the calibrated aperture E is opened to its fullest extent. The iris diaphragm K is then adjusted till the galvanometer G shows approximately zero deflection : the fine adjustment is next used till the deflection is exactly zero. The cell S_1 is then put in place of S_2 and the aperture E

is adjusted till the galvanometer deflection is again zero and the reading of the scale associated with E is read off on the drum.   Assuming that the light intensity has remained constant throughout, the currents given by D in each case have been equal to that given by F, so that D has been equally illuminated in each case : with the more absorbent solution with the shutter full open, and with the less absorbent solution with the shutter partially closed, so that there was less incident light.   The intensity-reduction produced by absorption in the first by partly closing the shutter is equal to that produced in the second and the ratio of the area of the partly closed aperture to the full aperture is a measure of the absorption.

Actually the results are unaffected by a change in the intensity of the light from the lamp during the series since both photo cells are equally affected.

The sensitivity is greatly increased by using a suitable filter, i.e. one which transmits only the range of wave-lengths over which the solution absorbs.   In using the apparatus the light source is only switched on while the measurements are being made, because prolonged exposure to red light causes the cells to behave irregularly : the precaution is actually unnecessary except with yellow and red filters, but it is advisable to make it the standard technique.

The apparatus can be used in exactly the same way for the measurement of turbidity.

Lovibond's Instrument.   In the Lovibond tintometer the colour of the solution is matched against the colour of standard glasses.   A complete set of glasses consists of 465, 155 of each of the colours, red, yellow, and blue. The glasses in each colour have a gradually increasing depth of colour, the deepest being designated a depth of 20 units, the others going from :

$$0.01 \text{ to } 0.20 \text{ by steps of } 0.01 \text{ units}$$
$$0.20 \text{ ,, } 0.90 \text{ ,, } \text{ ,, } \text{ ,, } 0.02$$
$$0.90 \text{ ,, } 2.00 \text{ ,, } \text{ ,, } \text{ ,, } 0.05$$
$$2.00 \text{ ,, } 5.00 \text{ ,, } \text{ ,, } \text{ ,, } 0.1$$
$$5.0 \text{ ,, } 11.00 \text{ ,, } \text{ ,, } \text{ ,, } 0.2$$
$$11.0 \text{ .. } 20.00 \text{ .. } \text{ .. } \text{ .. } 0.5$$

With glasses of equal strengths the red glasses transmit red, orange, and violet, and stop yellow, green, and blue light.

The yellow glasses transmit orange, yellow, and green, and stop red, blue, and violet light.

The blue glasses transmit green, blue, and violet, and stop red, orange, and yellow.

Combinations of red and yellow glass transmit orange only
   ,,   ,, yellow and blue ,,   ,,   green   ,,
   ,,   ,, blue and red   ,,   ,,   violet   ,,

while combinations of all three transmit no colour but only cut down the light and give a ' neutral tint '.   The comparator is very simple and consists of a wooden box with a partition down the middle and slots for slipping down the glasses.   The liquids are contained in open rectangular cells with plane glass ends and of various lengths from 0.0625 to 24 inches.   In using the instrument it is set up to face a diffuse white light, and its position altered

until the two fields appear to be equally illuminated. The cell containing the coloured liquid is then placed in front of one aperture and the standard glasses are tried in the slots of the other aperture until the colours match ; the number of units of each colour is then read off. Some coloured solutions are brighter than the standard glasses, and for these cases a series of neutral-tinted glasses are supplied which are used on the side of the liquid, while if the colour is duller than that of the standards, glasses of all three colours will be required to balance the colour of the solution ; the value of the least of the three colours is returned as black, e.g. the following glasses were used :

Red 3·2, yellow 15·2, blue 0·32

This gives black 0·32, and reduces the red to 2·88 and the yellow to 14·88.

But equal red and yellow glasses transmit orange only. Therefore the orange reading is 2·88 and ·the yellow 12·00.

The colour of the solution is therefore :

Black 0·32, orange 2·88, yellow 12·00

In another case the glasses were :

Neutral 0·16, red 8·0, blue 1·3

Hence light = 0·16. But blue and red transmit violet ; therefore the violet reading is 1·3 and the red 6·70, the colour of the solution being

Light 0·16, red 6·70, violet 1·3

The apparatus is used with such liquids as water, wines, spirits, oils, etc., and in addition can be arranged to measure the colour of solids such as flour and white lead, by reflection, such solids being pressed into small flat boxes and precipitated calcium sulphate being used as the standard.

For the application of the Lovibond tintometer to the determination of dyestuffs on cloth, see Green, *Analysis of Dyestuffs* (Griffin, London), 1920. The spectrophotometer (see chapter on the Spectrometer) may also be used for the determination of the percentage of colouring matter in a dyestuff mixture and also for the identification of particular dyestuffs.

Donaldson Trichromatic Colorimeter. This apparatus was designed at the National Physical Laboratory and is made by Hilgers : it is suitable for the measurement of colour of either transparent or opaque materials. The matching colour is synthesized by varying the proportions of three primary colours. The matched colour can then be expressed in the form and units of the Commission Internationale de l'Éclairage (C.I.E.).[1] Light from a lamp A, Fig. 43 (VI *) passes through three primary colour filters C : these are red, green and blue gelatine colour screens which comply with colorimetric conditions and are supplied exclusively by Hilgers. Over each filter is a movable shutter controlled by a knob so that the amount of each colour can be varied. After passing through the filters the light passes through the condensing lens B which forms an image of the source of light on the aperture J of the colour mixing box. This box is the hollow sphere D which is coated on the inside with a white diffusing layer of magnesium

[1] See Smith and Guild, ' The C.I.E. Colorimetric Standards and their Use ', *Trans. Opt. Soc.*, 1931–2 and 1931, **33**, 73–130 ; Judd, ' C.I.E. Standard Observer and Co-Ordinate System for Colorimetry ', *Journ. Opt. Soc. Amer.*, 1933, **23**, 259–374.

oxide : the diffuse reflection on this surface mixes the three primary colours to form light of a uniform colour which emerges from a second aperture K in the sphere and reaches the eye at E by the optical system shown, whereby the eye observes half of the field of the photometric cube G filled with light from the sphere. The other half of this field is filled with light from the specimen at X. The specimen is in an illumination box arranged so that it is illuminated by light from the standard lamp and shielded from stray light from the room. Opaque specimens are clamped at the back of the box and transparent ones mounted on a bracket provided for the purpose. A plate coated with magnesium oxide is included ; a colour match on this forms part of the routine use of the instrument. A mount for a double glass filter cell is also provided here : the standard lamp in combination with this cell and a liquid filter, the composition of which has been laid down as part of the International C.I.E. System of Colorimetry, forms the C.I.E. Standard Illuminant B representing mean daylight, while with another liquid filter and the standard lamp the C.I.E. Standard Illumi-

FIG. 43 (VI *)

nant C, corresponding to an average north sky light is obtained. The light from the specimen passes through lenses F and H which form an image of the specimen at E so that the structure of the specimen is not seen by the observer.

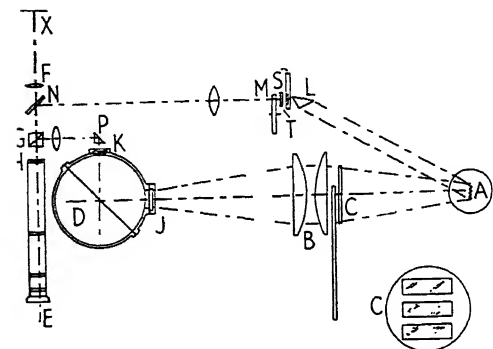For measurements on highly saturated colours, de-saturation of the specimen colour is brought about by light from the source A re-flected by prism L and transparent plate N. This light may pass through one of three colour filters (identical in colour with the primary colour filters at C) mounted on a rotatable wheel S, or alternatively through a hole in this wheel. The intensity of this desaturating light is varied by means of a circular neutral tint optical wedge M. A diffusing glass T is situated in the course of the beam.

The standard lamp is a 1000 watt lamp, aged and standardized at the N.P.L., the voltage being determined for which its colour temperature is 2848° K ; resistances and a voltmeter are supplied for maintaining constant potential difference at the terminals of the standard lamp and the colori-meter lamp. When the standard lamp is used without a filter it constitutes the C.I.E. Standard Illuminant A.

In making a measurement the operator varies the amount of the three primary colours by means of the knobs at C until a colour match is obtained and then reads the amount of each colour from the scales.

Nephelometry. Closely connected with colorimetry is the subject of nephelometry, which has been applied to the measurement of the concen-tration of suspensions in the estimation of proteins, fats, purines, ammonia,

phosphorus, chlorides, silver, etc.[1]   The Kober colorimeter (Fig. 41 (VI *)) is adapted to be converted into a nephelometer by the substitution of cups with transparent sides and black glass bottoms.   The lamp supplied with the instrument gives a parallel beam of light which falls laterally on the cups and is reflected upwards into the eyepiece by the individual constituents of the cloud of small particles forming the suspension.   The mirror M is of course not used.   With the longer tubes the zero is tested by inserting a test-piece of known length in the cups and bringing the cups up until they touch the plunger.   The nephelometer should be used in the dark room and similar precautions to those used in colorimetry should be taken, e.g. removal of dust and air bubbles, equality of illumination, correction of zero.   In using the nephelometer careful attention must be given to the correct conditions for producing and keeping the colloidal suspension.   As an illustration of the use of the instrument its application to the estimation of ammonia may be described.

To 80 grams of sodium chloride are added 130 ml. of ammonia-free water and 100 ml. of a cold saturated solution of mercuric chloride, with shaking.   When the salt is nearly all dissolved 70 ml. of a saturated solution of lithium carbonate (1 per cent) is added slowly while shaking, so that no mercuric oxide forms on the side of the flask ; 3 to 5 grams of talc powder are added, and after shaking the solution is filtered.   A stock solution of 1 per cent starch is freshly prepared for use.   Other solutions required are : ammonium sulphate, 100 milligrams per litre, and potassium sulphate, 75 grams per litre.

To make the standard ammonia solution, 10 ml. of the ammonium sulphate solution and 10 ml. of the potassium sulphate solution are made up to 100 ml.   For the standard cloud, 10 ml. of standard ammonia solution, 15 ml. of 0·003 per cent starch (a protective colloid), and 5 ml. of the mercuric reagent are mixed.   The solution to be tested is similarly treated with starch and reagent, the two solutions tested in the nephelometer cups for equal brightness.   For the application of the photocell to colour comparison, see page 261.   The measurement of turbidity and colour of liquids by an automatic electrophotometer has been described by Gollnow.[2]

[1] Kober, *J. Ind. Eng. Chem.*, 1918, *10*, 556.
[2] *Chem. Fabr.*, 1932, *20*, 161.

The British standard of candle-power is the Vernon-Harcourt pentane lamp. The candle-power of this lamp is given by the formula

$$\text{C.P.} = 10 \ \{1 + 0.0063(8 - e) - 0.00085(760 - b) \ \}$$

where b is the atmospheric pressure in millimetres of mercury and e is the humidity of the air in litres of water vapour per cubic metre of moist air. The 10 c.p. pentane standard is now used in France and the U.S.A., and is called the international candle. A sectional elevation of the lamp is shown in Fig. 44 (VI *).

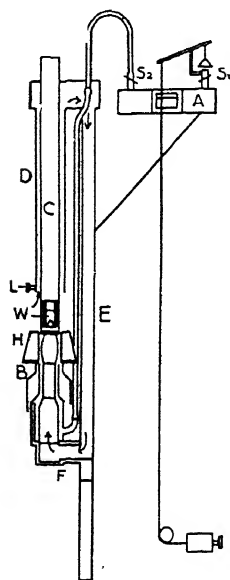The container is movable on its support and is filled two-thirds full of pentane, which can be observed by means of the window and is not to be allowed to fall below 0.125 inch. The air which enters the container through the cock S_1 is saturated with pentane vapour in A and passes through the cock S_2 to the flexible pipe K, and so to the burner B. This is a steatite ring pierced with thirty holes. Above the flame is the chimney C, in the side of which is a mica window W, on which is marked a horizontal line 88 mm. above the lower edge of the chimney. The flame is protected from draughts by means of the shade H. The chimney C is surrounded by a jacket D; when the chimney is hot a draught is created in the jacket and this causes warm air to be drawn up and, following the path indicated by the arrows, to pass down through the hollow pillar E, through F and so up through the centre of the steatite burner. In using the lamp the position of the lower edge of the chimney is fixed 47 mm. above the top of the burner by means of a gauge cylinder, and the chimney is centred by means of the three screws L provided for this purpose. The saturator A is placed on its support remote from the pillar E. When the flame has been lighted its height is adjusted by means of the taps S_1 and S_2 until the tip is halfway between the bottom of the window W and the mark thereon; after 15 minutes, if the flame height remains correct, measurements can be commenced. Any tendency of the flame to diminish is corrected by moving the saturator nearer to E. The part of the flame used is that visible horizontally through the shade H, the window W being turned away from the photometer. Distances are measured from the centre of the burner.

FIG. 44 (VI *)

The German standard is the Hefner amyl acetate lamp. The candle-power is given by the formula

$$\text{C.P.} = 1 + 0.006(8.8 - e) - 0.00011(760 - b)$$

where e and b are the same as for the pentane lamp.

The Hefner lamp is shown in Fig. 45 (VI *) and consists of a brass container C holding about 115 ml. Pure amyl acetate is used and the unused balance should be removed after use. The German-silver tube T is 25 mm. high, 8 mm. internal and 11 mm. external diameter. The wick consists of fifteen to twenty strands of untwisted cotton, and can be moved up by means of the screw S to adjust the flame height. G contains a lens and a ground-glass screen on which is a horizontal line 40 mm. above the level of the top of the tube T. The lens forms an inverted image of the tip of the flame on the screen and this image is made to touch the horizontal line.
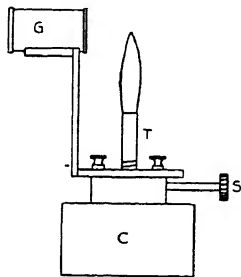
As sub-standards electric glow-lamps are used. These can be compared with standards at the N.P.L., and if used only for short periods remain constant for a long time. They are therefore almost universally used for ordinary photometric work. Since the candle-power of these lamps is so sensitive to changes of voltage (in metal filaments

to the fourth power, and with carbon filaments to the sixth power of the voltage), it is essential in accurate measurements to measure the voltage and maintain it constant. A battery of large capacity will give the most constant E.M.F., and a rheostat in the main circuit is used to control this. Potentiometer measurements across the lamp terminals and against a standard cell give the E.M.F., and if current measurements are also required a resistance capable of carrying the current without heating sufficiently to alter its resistance is included in the main circuit, and potentiometer readings are taken over its ends.

Photometers. For the comparison of light sources of the same colour the Lummer-Brodhun photometer is generally used. This is shown in
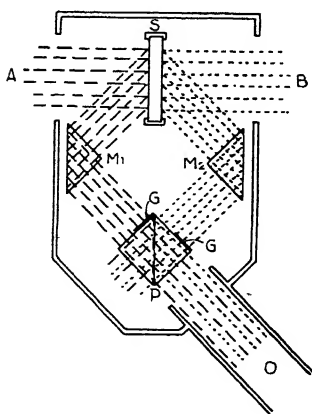

FIG. 46 (VI *)

Fig. 46 (VI *), which represents a horizontal section. The light from one source enters at A and that from the other at B. S is a white plaster screen having a flat matte surface. M_1 and M_2 are total-reflection prisms, and P is composed of two right-angled prisms; the hypotenuse face of the left-hand one has been sand-blasted with a geometrical pattern D, so that when the two halves are put together optical contact is obtained at the polished parts; hence light from M_1 will pass towards O only through the clear parts of D. Light from M_2 which strikes the clear parts of D will pass through P and so away from O, while that part of the light from M_2 which falls on the shaded part of D is totally reflected and passes towards O. The light reaching O therefore comes partly from A and partly from B, the shaded part in D being that portion of the light which comes from B. Now if the two surfaces of S are similar and are equally illuminated, the shaded and unshaded parts

of D will appear to be equally bright, and so the pattern will disappear. In practice, pieces of glass GG are inserted so as to reduce the intensity of the light over the rhomboidal patches by 8 per cent so that equality of illumination of S is judged by the similarity of contrast in the two parts of the field ; this field is brought into focus by means of the telescope O. S can be removed or reversed and shutters are provided at A and B to exclude dust when not in use.

In making a measurement the following procedure may be adopted : A comparison lamp of unknown candle-power is used on the right-hand stand and this stand can be fixed by means of a bar to the photometer head. First, the sub-standard is placed on the left stand and its filament plane is brought to right angles with the length of the photometer bench and accurately over the zero mark on the scale : with the screen S of the photometer head removed, the two lamps and the photometer head are aligned correctly. The candle-power of the sub-standard being known, the distance of the photometer head is adjusted to give an illumination of 10 metre candles on the screen. This distance in metres is the square root of one-tenth of the candle-power. The comparison lamp is next moved until equality of illumination is obtained, the mean of a series of settings by more than one observer being taken. The comparison lamp is then fixed to the photometer head by means of the clamping bar. The lamp to be tested is placed in the position previously occupied by the sub-standard, and to get equality of illumination the photometer and the comparison lamp are moved as a whole. When the setting has been made the candle-power of the test lamp is equal to the distance in metres, squared and multiplied by ten. The photometer head carries a bar on which are fixed a number of metal plates with apertures, so placed as to cut out stray light, and the bench is surrounded by dark curtains. An alternative method, when the candle-power of the test lamp is high, is to place this and the sub-standard at opposite ends of the bench and make the setting by moving the photometer head alone : if C_1 and C_2 are the two candle-powers and d_1 and d_2 the distances from the photometer,

$$\frac{C_1}{C_2} = \frac{d_1{}^2}{d_2{}^2}$$

Since the best results are obtained when the illumination of the screen is about 10 metre candles, with a very high candle-power it is convenient to cut down the light by means of the rotating sector disc. This consists of two discs from each of which three equal sectors have been removed. The discs are rotated by means of a motor, and the relative positions of the two discs can be varied while the apparatus is in motion. The light transmitted is equal to the total angular opening divided by 360°.

Polarization Photometers. An example of this type of photometer is the Martens instrument shown in Fig. 47 (VI *). Here the standard and the test lamp are placed in turn at the same fixed distance from the matte white plaster screen at F. The path of the light from the screen is shown by the broken line. After total reflection at P and Q it passes through the Wollaston prism W, the biprism B, and the Nicol prism N to the eyepiece.

The comparison lamp is the glow-lamp shown at G which illuminates the opal glass screen *b*. The path of this light through the prisms W, B, and N to the eyepiece is shown by the dot-and-dash line.

The prisms W and B are placed so as to polarize the two beams at right angles. The nicol N can be rotated, and its rotation observed on a graduated scale. By this rotation the intensity of one beam is increased and that of the other reduced, so that equality of the two halves of the field can be obtained. The relative candle-powers of two lamps placed successively at right angles is given by

$$\frac{C_1}{C_2} = \frac{\tan \theta_1{}^2}{\tan \theta_2{}^2}$$

where θ is the angle of rotation of the Nicol prism from its zero position.

With all lamps the candle-power varies with the direction of measurement, and these variations are recorded on a polar diagram. Measurements are usually made in a horizontal plane through the axis of the lamp and in a vertical plane containing this axis. To take the former case, the lamp may be fitted in a holder capable of rotation and with means for measuring that rotation. The lamp is rotated by steps of 10° and measurements of the candle-power made for each position. These results are plotted along the radii of a circle also spaced at 10° and the points so obtained are joined up by a curve.

Rotators are also made for rotation in the vertical plane. Some light sources cannot be rotated in a vertical plane without alteration of their candle-power, and with these an arrangement of movable mirrors is used. The mean horizontal candle-power can also be obtained by rotating the lamp at a speed of 120 revolutions per minute while the measurement is made, the current being led in by leads travelling in circular mercury troughs. The method gives unsatisfactory results with gas-filled lamps.

FIG. 47 (VI *)

Hock has used a photometric process to compare the colours of various specimens of carbon black. The specimens were mixed with (*a*) 100 parts of lithopone and (*b*) 'rubber and zinc oxide'. Each mixture was compared with pure lithopone and with 'rubber-zinc oxide' mixture, by measuring the relative intensities of reflection of light by means of a Marten polarization photometer for measuring blackness or by use of a leucometer [1] or by use of a modification of the unimeter of Bloch. The method is also applicable to the quantitative measurement of the colour imparted by various pigments to rubber mixtures.

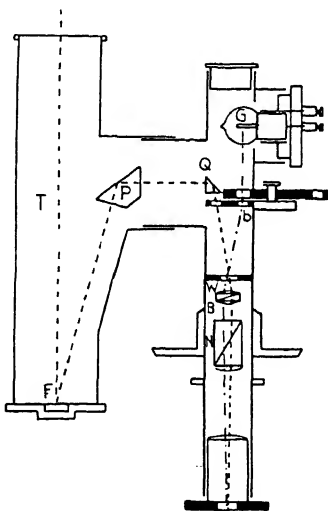**Hetero-chromatic Photometry.** When the colour of the light from

[1] Manufactured by Schmidt and Haensch, Berlin.

two sources is not the same it is difficult to make measurements of any accuracy by means of the methods already described. If, however, the two illuminated surfaces of the photometer are not seen by the eye at the same time but in turn.in rapid succession, a flickering appearance is seen when the two surfaces are not equally bright, and this flicker disappears on equality being obtained, even though the colour of the light from the two sources is not the same. This principle is made use of in the Simmance-Abady flicker photometer. In Fig. 48 (VI *)a let ABCD and EFGH be truncated

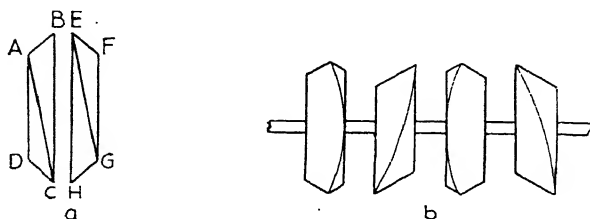FIG. 48 (VI *)

cones of plaster. If the parts ABC, FGH are removed and DAC and EFG are placed in contact, a disc of the required form is obtained. Fig. 48 (VI *)b shows four of these discs mounted at angles differing by 90°. When this apparatus is rotated and is illuminated from the two sides, the line separating the two sides will move across the field of vision and back again once for each rotation of the discs, and the flickering field will be obtained. When the relative brightness of the two surfaces is the same no flicker will be observable even at slow rotation frequencies.

SECTION 7 : MICROPHOTOMETRY

Thermovacuum Microphotometer. The microphotometer is used for the investigation of the intensities of photographed spectral lines.[1] The plate is fixed in a holder and a beam of light from an incandescent lamp passes through the plate and falls on a vacuum thermocouple. A moving coil galvanometer is placed in series with the thermocouple and the deflections of the galvanometer, which depend on the intensity of the lines on the portion of the plate exposed, are photographically recorded on a sheet of bromide paper stretched round a drum. By moving the plate-holder slowly and at the same time rotating the drum, a record is made showing all the details of the spectral lines under examination. The principle of the apparatus made by Kipp and Zonen is shown in Fig. 49 (VI *). An
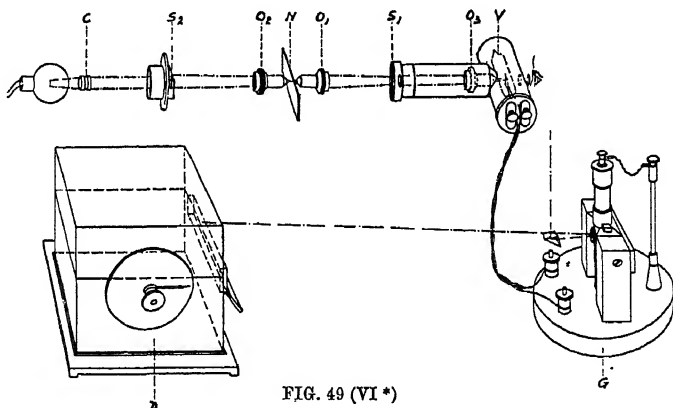

FIG. 49 (VI *)

image of the filament of a small incandescent lamp is projected on the slit S_2 and the objective O_2 throws a greatly reduced image of the slit on the photographic plate. A second objective forms an enlarged image of the illuminated part of the plate on the slit S. The light transmitted by S is concentrated on the vacuum thermocouple V by means of a third objective O_3. The vacuum thermocouple employed is specially designed for rapid response, so that the recording of a spectrum with hundreds of lines can be made in a few minutes, a special Moll microphotometer having a short time of indication is used in series with the thermocouple.

In the apparatus designed for accurate microphotometry by Kipp and Zonen,[2] the plateholder is mounted on a slide and has a transverse displacement of 6 cm., controlled by means of a micrometer screw. It also has a vertical displacement of 5 cm. so that several spectra on one negative may be recorded successively without readjustment of the instrument.

[1] Moll, *Proc. Phys. Soc.*, 1921, *33*, iv.
[2] Kipp and Zonen, Delft, Holland Reference Leaflet MF29.

The drum is rotated by means of the same shaft which carries the micro-meter screw displacing the negative. For this purpose two different gears are mounted on this shaft so that if the drum is connected to one gear, 1 mm. displacement of the plate corresponds to 50 mm. of the drum peri-phery. The other gear gives a ratio of 1 : 7. The sheet of bromide paper on the drum measures 12 × 40 cm., these 40 cm. corresponding either to 0·8 or to 5·8 cm. of the photographic plate.

A 1/30 h.p. electric motor connected to a reduction gear forms the driving mechanism.

Photoelectric Microphotometers. Other recording microphoto-meters have been described in which photoelectric cells have been employed instead of thermovacuum elements. For obtaining the necessary sensitivity it is necessary to employ gas-filled cells in conjunction with some form of electrometer (usually of the Lindemann type). Such an apparatus is open to two serious objections. In the first place, no gas-filled cell is steady enough for use in precision work, and secondly, it is not possible to obtain a small and well-defined light spot from an electrometer. A recording
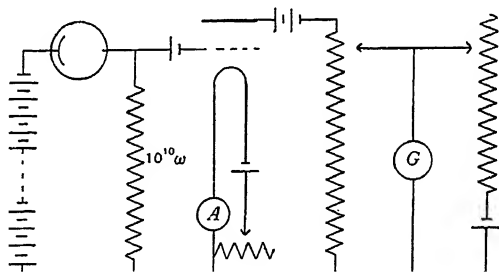

FIG. 50 (VI *)

microphotometer in which these objections are eliminated has recently been described by Lees.[1] In his microphotometer a vacuum cell is used with one stage of valve amplification and an ordinary galvanometer.

The photoelectric cell is a Phillips vacuum potassium cell, type 3570, with a sensitivity of 4 micro-amps. per lumen. The photoelectric cell is inserted in the grid circuit of a Philips electrometer-triode with a xylol alcohol (3 × 10⁹ ohm) grid leak and a − 2V grid bias. This valve has a grid insulation resistance of 10¹⁴ ohm. The xylol alcohol leak consists of a 5-cm. pyrex tube of 4 mm. internal diameter containing a 10 : 1 mixture of xylol and alcohol with tungsten electrodes. The anode current from the valve is balanced by the adjustment of the resistance in the shunt circuit as shown in Fig. 50 (VI *).

In ordinary use the maximum light falling on the cell is 1×10^{-5} lumen, giving a photoelectric current of 4×10^{-11} amp. This, if a grid leak of 10×3 ohms is used, alters the grid potential by 0·12 volt and the correspond-ing change of anode current is 6 micro-amps., which is ample to give a large deflection in quite an insensitive galvanometer. The optical and mechanical arrangement of the microphotometer designed by Lees are fully described in the original paper. Lees claims considerable sensitivity and also a rapidity

[1] J. H. Lees, *J. Scient. Inst.*, Vol. VIII, No. 9.

of action corresponding, in the simple case, of a continuous spectrum to a speed of 10 mm. per minute.

Non-recording Photoelectric Microphotometer. Messrs. Hilger make an instrument of this type which is used for emission work or with modification for measurements on absorption spectra.

Fig. 51 (VI *) shows a simplified diagram of the apparatus as arranged for the former purpose. Here L contains the source of light which is a 6 volt 18 watt motor headlamp, with directly soldered connections and running from a battery. The prism P reflects the beam at right angles up to a 25 mm. microscope objective, M_1, below the stages ; this forms an image of the lamp filament on the plate which is placed on the stage S with
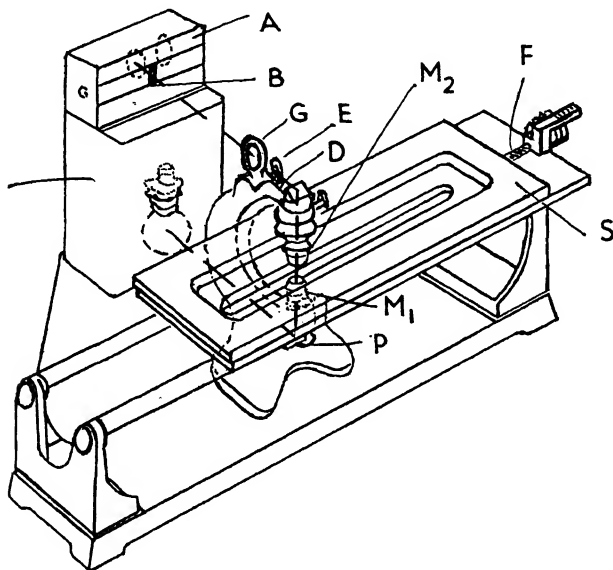

FIG. 51 (VI *)

the film side uppermost. The linear dimensions of this image are one-tenth of those of the filament.

The second objective, M_2, forms an image of the plate on the slit B, which is in the centre of the screen A. The magnification of this system is ten times : the image of the plate is thus magnified ten times while the image of the filament is its actual size (since it was reduced one-tenth by M_1).

Behind the slit is mounted a photoelectric cell of the rectifier type. Between L and P is the ' viewing lens ' (not shown), which can be pushed into the beam when required.

The plate stage, taking any plates up to 10 × 4 inches, runs freely on guides and can be traversed quickly from one end of the plate to the other. It can be clamped in any position and the screw F, 25 mm. long and reading to 0·01 mm., then comes into play and by its use the plate can be traversed accurately over any distance up to 25 mm.

The ' cross-slide ', an additional stage (not shown), is mounted on stage S and is movable in the direction of the length of the spectrum lines. A

mechanical means is incorporated for setting the plate accurately with respect to the optical system. When the plate is set for one exposure, a manual displacement of the stage on the cross-slide puts further exposures in the correct position.

An automatic device can be fitted for moving the plate by steps of 2 mm. or other fixed distance : the use of this requires that the successive spectra should be photographed at the same distance.

To take readings the plate is placed on the slide, film face uppermost, and the ' viewing lens ' is put in position : the plate is illuminated with a patch of light and an image of the spectrum is thrown on the screen A. The stage is set so that the image of the required line falls parallel to the slit and the plate is traversed by the screw F until the line falls exactly on the slit. The ' viewing lens ' is now pushed out of the beam, whereby the light from the filament after passing through the spectrum line is focused on the slit and falls on the photoelectric cell. The amount of light transmitted by the spectrum line under examination is shown by the difference of the galvanometer reading when the light is excluded from, and allowed to fall on, the photo cell. This light is then compared with that transmitted by some other part of the plate, which may be the image of another line, of the background of the spectrum, or the clear unexposed part of the plate.

Normally the length of spectrum line illuminated is about 0·7 mm.; this may be increased to 2 mm. by the interposition of a cylindrical lens incorporated on the same mount as the ' viewing lens '.

To measure the light transmitted a rectifier type of photo cell is used. This has the advantage that it is so sensitive that the current given can be measured with a galvanometer without amplification and no battery is required : in addition it responds almost solely to visible radiation so that ordinary objectives can be used for the optical system. The galvanometer used should have a resistance of not more than 500 ohms and a sensitivity to detect 10^{-9} amps.

The slit B has one jaw fixed, while the other is movable by means of a screw. The width of the slit can be set by the aid of a vernier device to a series of values between 0·05 mm. and 0·25 mm., in steps of 0·05 mm. and can be made correctly to within 0·01 mm.

Modification for Absorption Measurements. The apparatus described above is adapted for this purpose by means of two attachments. The first is a photo cell unit containing two photo cells and a simple optical arrangement; the second is the ' equaliser ' which fits on the arm holding the microscope objectives.

With an absorption plate on the stage and the ' viewing lens ' in position an image of a pair of spectra, separated by a narrow dividing-line is thrown on the screen. The light forming the image of one of these falls on one photo cell, that from the other on the second photo cell. A horizontal line is engraved through the centre of the slit and at right angles thereto and the plate is to be placed so that the image of the dividing line between the spectra falls on this line and remains thereon when the plate is traversed.

The photo cells are connected so that when equal amounts of light fall on them no current passes through the galvanometer. To determine the match points the plate is set so that a clear part near the spectrum to

be matched is imaged on the slit. The currents given by the two cells are then made equal by means of the 'equaliser', which displaces vertically on B the image of the filament of the lamp until the proportion on either side of the dividing-line is such as to give equal currents.

When the plate is correctly set on the stage so that the line dividing the two spectra falls exactly on the engraved line, the 'viewing lens' is displaced and the match point found by traversing the stage by means of the screw, until the deflection of the galvanometer becomes zero : the match point is then the point imaged on the slit.

The apparatus is most useful when the light source gives a continuous spectrum.

Messrs. Bolton & Williams (London) make a technical photoelectric absorptiometer in which the light source is an electric lamp connected directly to the mains. The light passes through a condenser to an adjustable slit and then to a cell containing a 1 per cent solution of copper sulphate for the absorption of the infra-red rays, and next through a selected Wratten filter. The light passing through the filter falls on a photoelectric cell which is connected directly to a galvanometer, the scale markings on which are reversed, reading from 100 to zero. In testing a liquid the slit is first adjusted till the scale reading is zero (i.e. full current is passing), and this represents zero absorption (no current, marked by 100 on the scale, represents 100 per cent absorption). The liquid, contained in a standard sized cell, is placed between the Wratten filter and the photo cell and the position of the needle represents the percentage absorption of the light of the wavelength transmitted by the filter.

In the Central Scientific Company's instrument the arrangement is very similar, except for the omission of the copper sulphate cell. Care is taken to get a constant intensity of the light source by the use of a 6-volt lamp operated by a transformer of constant power output, and a very sensitive low-resistance Weston microammeter is used to measure the current.

SECTION 8: PHOTOELECTRIC EFFECT

In 1888 Hallwachs observed that a negatively charged metal rapidly loses its charge when ultra-violet light falls upon it. A well-insulated, uncharged substance acquires a positive charge under similar circumstances. The more electropositive the metal, the more marked is the effect produced. This property is not peculiar to the metals. It is exhibited by salts, especially by metallic sulphides, while a large number of organic substances, such as dyes and other benzene derivatives, are found capable of giving considerable photoelectric discharges. The discharge obtained from anthracene, for instance, is of the same order as that given by zinc. This photoelectric effect was applied by Elster and Geitel in 1905 to the measurement of visible light.

The photoelectric capacity of a substance is a constitutive property unlike secondary radiation, excited by Röntgen radiation (Barkla), or radium radiation (McClelland), which is additive in character. Hydroquinone gives a considerable photoelectric discharge, while its isomer resorcin is practically inactive. The amount of photoelectric discharge produced under given circumstances has been found to vary with the degree of molecular compactness of the material, crystalline form, &c. Fused anthracene is found to be more active than the crystalline substance.

The determination of photoelectric effect has been applied to a considerable extent in the case of problems dealing with fluorescence and phosphorescence. Stark's theory of fluorescence and Lenard's theory of phosphorescence are both based mainly on the photoelectric activity of fluorescent and phosphorescent compounds. Stark and Steubing investigated the photoelectric discharges of a large number of fluorescent organic substances. They found that the absorption of light in absorption bands shaded towards the red is accompanied both by the photoelectric effect and also by fluorescence. They concluded from their results that photoelectric effect and fluorescence are quantitatively related. Lenard and Klatt, by using light filters, found that the light which did not produce phosphorescence did not produce photoelectric effect.

There is a definite maximum wave-length characteristic of each substance at which the photoelectric effect begins. The relation between the total photoelectric discharge and the intensity of the exciting light appears to be linear. Both the magnitude of the discharge and the velocity of emission are independent of temperature. Zinc and aluminium give a measurable effect in sunlight, but copper, lead, platinum, iron, carbon and mercury require light richer in ultra-violet rays. The more electropositive metals are specially active and lose a negative charge in diffused daylight.

It appears somewhat unlikely that the majority of photochemical reactions are directly related with the photoelectric discharge. Pauli,[1] in

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[1] *Ann. Physik*, 1913, *40*, 677.

dealing with a number of fluorescent substances, for instance, found that in no case did visible light produce a photoelectric effect, while, in all the compounds chosen, the light most efficient in producing fluorescence was in the green or blue. Moreover, the photoelectric effect always increases with decreasing wave-length, while this is not the case with fluorescence. With anthracene the region producing fluorescence ($\lambda 4,000$–$\lambda 2,250$) does not produce photoelectric effect. While fluorescence and photoelectric effect may not be directly connected, experience indicates that it is easier to separate an electron from a fluorescing than from a non-fluorescing molecule.

The fluorescence of chlorophyll has been measured by Franck and Wood, as follows. The fluorescence was excited with blue light, emitted by a 750-watt tungsten lamp, filtered through cuprammonium solution and focused by two large condenser lenses, on the underside of the leaf containing the chlorophyll. A total-reflecting prism was used to deflect the converging cone of rays through a right angle in order to permit observation of the fluorescence in a direction perpendicular to the surface of the leaf. The blue patch of light on the surface of the leaf was observed through a red filter and the red fluorescence measured with a small photometer, which allowed exact comparisons with a beam of another source of red light whose intensity could be varied. The calibration curve of the photometer was obtained with the aid of an optical bench. The red filter cut off all blue light reflected and scattered by the leaf, so that only the intensity of the red fluorescent light was measured.

Photoelectric Fatigue. The photoelectric discharge obtained from a given substance is frequently found to undergo considerable variation. The photoelectric power of a recently exposed surface is usually found to decrease with time. This diminution in activity may take place when the substance is kept in the dark ; on the other hand, it is frequently found that when inactivation results from illumination, recovery may even take place in the dark. The phenomenon is known as photoelectric fatigue, and no satisfactory general explanation has so far been advanced to deal with it.

Knoblauch suggested that fatigue was due to chemical change such as oxidation ; yet it is found to take place *in vacuo*, and oxides, such as lead peroxide, show fatigue in much the same manner as the metals. Lenard suggests that it is due to the formation of an electrical double layer. Anthracene only shows fatigue when the exposed layer exceeds a thickness of ·02 mm. Since anthracene is a good insulator, a thicker layer would easily accumulate a positive charge on the surface. On the other hand, good conductors, such as the metals, also show fatigue. Ramsey and Spencer attributed fatigue to the disintegration of the metal owing to the expulsion of electrons by light. Lenard's observations on the apparent disintegration of carbon by light *in vacuo* is of interest in this connection. Hallwachs attributes fatigue to a change in the surface film of gas.

Determination of Photoelectric Effect. The current produced when light falls on a substance, the potential of which relative to the surrounding medium is favourable to the escape of electrons, may be regarded as a measure of the photoelectric effect. The actual determination of the total photoelectric effect which a substance is capable of producing is attended with very great experimental difficulty ; so much so, that attempts to

arrange the metals in the order of their photoelectric activities have not led to really consistent results.

There are two general methods in use for the investigation of the photoelectrical effect. In the first of these the potential of the illuminated plate is determined by connecting it to an electroscope or electrometer, all bodies in the neighbourhood being kept at earth potential. The plate acquires a positive potential owing to the emission of electrons from its surface. The maximum positive potential X acquired is noted, and this is a measure of the maximum energy of the electrons leaving the plate. If $\frac{1}{2}mv^2$ is the energy of the electrons, then $Ve = \frac{1}{2}mv^2$, from which the maximum velocity v of the electrons may be determined.

The second method of measurement provides a means of finding the number of electrons leaving the plate. In this case the illuminated surface forms one plate of a condenser, the other plate of which is a piece of wire gauze, so that light from the source can pass through this grid and fall on the active surface. In all such work the illuminated plate and grid are mounted in a highly evacuated tube. The grid is connected to the positive terminal of a battery, the plate being connected to the negative, and the photoelectric current is measured by a sensitive galvanometer placed in the circuit. The photoelectric current depends on the number of electrons leaving the surface per second and it is possible by varying the applied potential to find how the number depends on the applied field. By reversing the direction of the potential the escape of the electrons from the illuminated plate is retarded and only those possessing a limiting velocity will reach the grid. By plotting the current against the applied potential a ' velocity distribution ' curve may be obtained from which the proportion of electrons leaving the plate with any given velocity may be found.

Experimental Results. Two results of considerable significance have been obtained by the above methods :

(1) The number of electrons leaving an illuminated surface in unit time is directly proportional to the intensity of the incident light.

(2) The maximum of energy electrons released at a photoelectric surface is independent of the intensity of the incident light, but is directly proportional to the frequency of the light.

These facts are not explicable by the ordinary classical laws of radiation, and in 1905 Einstein proposed that the phenomena of photoelectric emission could be accounted for by adopting Planck's Quantum theory of radiation (see chapter on Raman Effect), and assuming that when a quantum of radiant energy $h\nu$ reacted with an electron, the electron acquired the whole quantum, being thereby released from the active surface with an equivalent amount of kinetic energy.

Einstein's equation is

$$h\nu = \tfrac{1}{2}mv^2 - w_0$$

where h is Planck's universal constant of radiation, ν is the frequency of the incident light, and w_0 is the amount of work done when an electron escapes from the atom to which it is attached.

This equation possesses a high degree of generality for it applies to radiation of all frequencies. It has been experimentally verified by Millikan

to a high degree of accuracy, who has shown that this furnishes one of the best methods of determining Planck's constant.

Uses of Photoelectric Cells. A great number of miscellaneous applications of the photo cell have been introduced. From the physico-chemical point of view a few selected examples are given below which serve as interesting illustrations of the type of operations that can be performed.

Measurement of turbidity. The turbidimetric titration of small amounts of nicotine (using the silico-tungstic acid test) can be made utilizing a photo-electric apparatus with a Spencer titration cell. The method can also be used in the determination of other substances where a good precipitate reaction can be found.[1]

Colour Matching. The photoelectric cell is ideally suited to the matching of colours, the equipment employed being the same as that used in standard colour-matching devices, except that the photoelectric cell is substituted for the human eye. Light is focused upon a specimen, and is then diffusely reflected through a filter on to the cell. The photoelectric currents are observed for different specimens and with given filters, those for which the currents are the same with the different filters being identical in colour.

Colour Analysis. A simple recording colour analyser has been described.[2] The specimen is placed at the centre of a luminous hemisphere and the light reflected from it passes to the photo cell through a monochromator. One slit is adjusted in width to correct for variable dispersion of the prism, the other being adjusted in length to compensate for the colour sensitivity characteristic of the cell.

The analyser is calibrated with a standard and the reflectivity of a specimen photographically recorded on a plate.

Sunlight Integration. A method of integrating the light emitted from a given source, in which a cell is used in series with a battery and a hydrogen voltameter has been developed. The total quantity of electricity passed to the cell is accurately recorded by the volume of hydrogen liberated at the cathode. A modification of the method in which a copper voltameter is used has been described by Atkins and Poole [3] and by Teegan and Rendall.[4]

The photoelectric cell used was a Burt sodium cell.

Automatic Controls. The fact that the colour response of a cell is not ordinarily flat is used in quantitative chemical industrial measurements upon coloured liquids. The photoelectric cell can be applied to automatic titration work.

Photometry. The photo cell has been extensively employed in visible and ultra-violet photometry. Harris has described a photometer for measuring the intensity of ultra-violet radiations, in which a cadmium cell is employed, the photoelectric current being amplified by a valve amplifier so that comparative measurements can be made with a micro-ammeter.

[1] Goodhue, *Ind. and Eng. Chem. An.*, 1938, *30,* 52.

[2] A bibliography on photoelectric colorimetry is given by Turrell and Waldbauer, *Iowa. Acad. Sci. Proc.*, 1935, *42,* 63–70. See also Kimble, *J. Lab. Clin. Med.*, 1939, *24,* 1055.

[3] Atkins and Poole, *Roy. Soc. Phil. Trans.*, 1936, 235A, 245.

[4] Teegan and Rendall, *Ind. J. Phys.*, 1930 (4), *7,* 585.

Numerous instruments suitable for the comparison of luminous intensities have been described, and the application of the photo cell to microphotometry has been referred to in another section of the book.

In dealing with problems within the sphere of physical chemistry a method which would give *relative* photoelectric discharges is all that is usually required. A paper on the photoelectric effects of phototropic compounds by Gallagher [1] describes a simple, convenient apparatus which was found to give very consistent results at atmospheric pressure. The apparatus consists of a small gold-leaf electroscope which is mounted in front of a mirror (Fig. 52 (VI *)). The mirror bears a scale by means of which the position of the leaf of the electroscope may be read off at any instant. The electroscope is connected with an insulated copper plate G, over which is spread a fairly thick layer of the substance under examination. A mercury lamp serves as a convenient source of light. Care must be taken that the light from the lamp falls only on the substance under examination. All other parts of the apparatus are protected by means of a wooden cover or box which is provided with a small window (W) for the illumination of the substance. It is very advisable to mount the whole apparatus in a case so that the connections may be protected from variations in atmospheric humidity.

When the electroscope has been charged negatively and a substance on the plate exposed to ultra-violet light, the rate of discharge of the electroscope over a given number of divisions of the scale will depend on the photo-

FIG. 52 (VI *)

electric power of the substance, provided, of course, that the light intensity is constant. In the case of many organic compounds examined, however, a remarkable fatigue sets up once the illumination of the substance has begun; it having been found that the discharge falls off rapidly towards zero in certain cases. The following procedure enables one to study this fatigue :
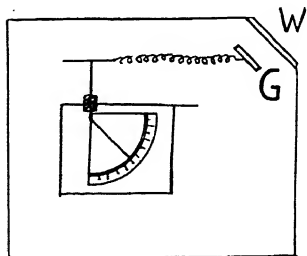
The electroscope is first charged so that the leaf is above the first division on the scale. The substance is then exposed, and the time noted with a stopwatch. The time is again noted when the leaf passes the first scale division, and again when it passes the second. The electroscope is then recharged without interrupting the illumination, and the times at which each of the two scale divisions are again passed are again noted. The operation is further repeated as often as may be necessary. With the results obtained curves may be plotted showing the variation of photoelectric effect with the period of illumination of the substance. For further details of the procedure to be adopted the reader may be referred to the original memoir.

The arrangement involving the use of a galvanometer, as already mentioned, would have many advantages over the use of an electroscope in this type of work, but the electroscope apparatus is exceedingly simple in construction and excellent in its way, in comparative work. By means of this apparatus it was found that, as a rule, phototropic substances show much

[1] *Bull. Soc. Chim.*, 1921 (4), *29*, 683, and 962.

more gradual fatigue than chemically related non-phototropic substances. A necessary precaution consists in ensuring uniform illumination throughout a series of experiments. The mercury lamp does not give a constant light until it has been burning for some time.

The Zeleny Electroscope. A more recent type of electroscope may be described here. In the ordinary deflected leaf electroscope the rate of fall of the leaf is measured and the leaf must be recharged before each test. In the Zeleny instrument [1] the leaf is automatically charged to a definite potential by striking a charged plate and the experimenter, instead of measuring the rate of collapse of the leaf, observes the frequency with
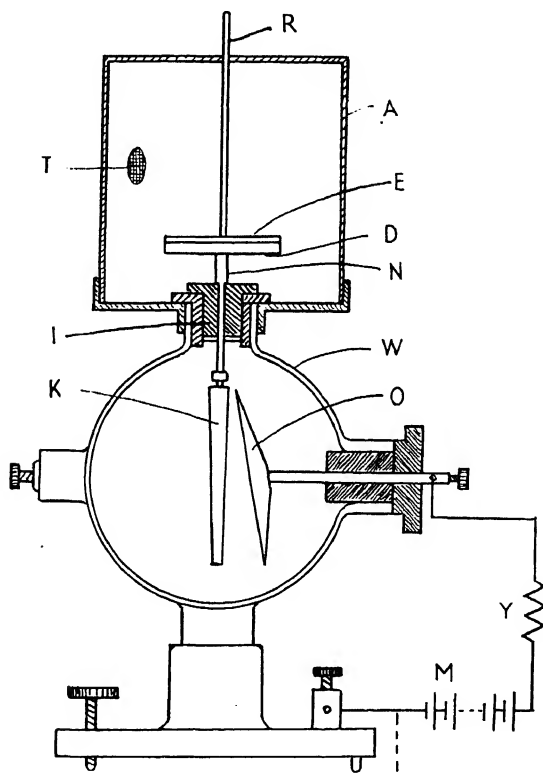

FIG. 53 (VI *)

which the leaf strikes the plate. The use of a microscope for observing may thus be dispensed with. The instrument is shown in Fig. 53 (VI *). The leaf K, suspended from a hinge at the lower end of the stud N, swings freely in the plane of the page and makes contact with the plane O. N is rigidly mounted in the case W with amber insulation at I; N is surmounted by the platform D. An ionization chamber A is attached to W. O is held at a potential of 50–200 volts above that of W (and A) by a battery M. A resistance of one megohm, more or less, is inserted at Y in order to protect the leaf in case of short circuit. R is a rod with a disc at its lower end

[1] *J. Phys. Rev.*, 1911, *32*, 581.

which rests on D.   R projects through a hole in the top of A without touching A and is the means of connecting the leaf system to other apparatus when the capacitance is measured.   Now if the space between D and A is made conducting, the charge on K leaks away, the potential falls and K moves towards O.   Finally K strikes O, whereupon it is recharged and repelled by O.   The fresh charge on K begins to leak away, and the cycle thus completed is repeated indefinitely.

Measurement of Ionization Current.   Let K be slowly oscillating due to an ionizing current : the potential of K will be equal to that of the plate O at the moment of touching : call this potential E_1.   A is now repelled, the charge leaks away and just before K again touches O the potential has fallen to E_2.   The quantity of electricity transferred from the plate to the ground via the leaf system, for one oscillation of the leaf, is $C_z(E_1 - E_2)$ where C_z is the capacitance of the system.   If p is the time of one oscillation, the ionization current I is given by

$$I = \frac{C_z(E_1 - E_2)}{p}$$

E_1 is the potential of the battery M. C_z may be found by the method described by Barton.[1] p is determined with a stop-watch. E_2 is found by applying a known potential to K by way of R, from a potential divider circuit.   This potential is of the same sign as that on O and is gradually lowered till K touches O. $(E_1 - E_2)$ and also C_z is a function of the leaf-plate separation and so this must not be disturbed after E_2 is measured.

(The makers can also supply an accessory ionization chamber and leaf system connector with the aid of which ionization currents may be measured without determining C_z.)

Photoelectric Cells.   The general principle of the photoelectric cell depends on the fact that short-wave light on coming in contact with potassium or its hydride, causes electrons to be emitted and they conduct electricity across the vacuum to the positive.   The photoelectric cell is connected through an electrometer with a battery of 100 volts and the readings on the electrometer are proportional to the intensity of light. If necessary the current may be increased by valves.   For details original papers should be consulted.[2]   The photo cell is useful in the measurement of relative intensities but the photo-current is not exactly proportional to the incident intensity and each cell requires separate calibration.

For nearly all present applications of photo cells only visible light is employed, so that ordinary glass is used for the walls.   Because of ease in working soft 'lime' glass is used—common lead glass being unsuitable as it is rather readily attacked by alkalies.   The usual form of cell is the central anode type, in which the positive grid or ring is situated near the geometric centre of the axis of the cell.   The negative electrode which comprises the sensitive cathode completely surrounds the anode, and may assume the form of a coating on the inner wall of the cell or may be a flat or semicircular

[1] *Rev. Sci. Inst.*, 1932, 3.
[2] Forbes, *J. Phys. Chem.*, 1928, *32*, 482.   See also Perry, *Chemical Engineers' Handbook*, McGraw Hill, 1934 (Photo-sensitive Cells, p. 1718).

plate coated with the active substance. The metals usually employed are sodium, potassium, caesium and barium. The methods of depositing the metal are by distillation, by electrolysis or by disintegration. Photo-electric cells are in general of two types : vacuum and gas filled. The former are usually employed for photometric measurements, since the photoelectric current is closely proportional to the intensity of the light entering the cell. Gas-filled cells have the advantage of giving a larger photoelectric current (due to ionization) for a given light intensity, but they are not by any means so linear in their response to light of varying intensity as the vacuum type.

Thermionic Valve. Fleming's valve consists of two separated elec-trodes fixed in a vessel which is evacuated. The cathode or filament supplies free electrons. The anode is kept at a positive potential with respect to the cathode and free electrons are attracted to it and thus an electrical current can pass across the vacuum. In physico-chemical work the valve in various modifications is being applied to magnify extremely small currents and for rectification. Numerous circuits have been devised in this direction, and this subject is considered in more detail in the next chapter.

Sources of Ultra-violet Light. In the determination of photoelectric effect the most convenient sources of ultra-violet light are the quartz mer-cury lamp or a spark between aluminium terminals. The line $\lambda 2,540$ of the mercury lamp is particularly effective because of its great intensity and its situation well in the ultra-violet.

A discharge in hydrogen at a pressure of 1–5 mm., though feeble in the visible spectrum, is said to give a photoelectric discharge from zinc over 200 times greater than that obtained with a mercury lamp.

Efficiency of Ultra-violet Light. The measurement of the efficiency of the ultra-violet light source may be carried out by means of some photo-chemical reaction.[1] These reactions only proceed between certain closely associated limits of wave-lengths and some work has been carried out with the object of referring the principal photochemical methods of studying ultra-violet energy to their particular region of the spectrum by direct spectrographic means. The decomposition of oxalic acid when catalysed by uranyl salts, and potassium iodide decomposition were studied.

The method as applied in one of the experiments is as follows : 2 ml. of a solution containing 6·3 grams of oxalic acid and 4·27 grams of uranyl sulphate per litre are exposed to the rays in a stoppered quartz test tube, which is supported in the focal plane of a spectrograph. The contents of the tube are then washed out with water into a flask, acidified with sulphuric acid, and titrated against 0·02N-potassium permanganate.

The spectrographic system consisted of two quartz lenses of 4·45 cm. aperture and 25·4 cm. and 50·8 cm. focal length, and a 60° quartz prism to correspond. These were mounted in a wooden casing, with the prism in the minimum deviation position. An adjustable slit, in which the leaves moved symmetrically about a fixed centre, was used. The plate carrier was adjustable for focus, and was adapted to hold a rack of test tubes or a fluorescent screen and slide. All these lie in the same focal plane.

[1] *If a photoelectric cell sensitive to the ultra-violet light is available, it may also be used to measure the efficiency.*

The ideal source of light for this work would be one having a continuous spectrum of high intensity. A practical approximation to this ideal is obtained in the mercury arc, the radiation from which, although characterized by well-defined lines, also yields a continuous spectrum of moderate strength. A mercury-vapour lamp of the vacuum type, consuming 2·5 amps. at 100 volts, was therefore used. A control rheostat was included in the circuit to ensure that the current was maintained at a steady value.

The spectrograph was mounted with its slit parallel to the axis of the mercury arc, which was inclined at 20° to the horizontal. Two quartz condensers of 7 cm. diameter forming a system of focal length 2·85 cm. fixed at a distance of 5 cm. from the arc, were employed to concentrate its light upon the slit. The test-tubes were of fused quartz, glass-stoppered, of
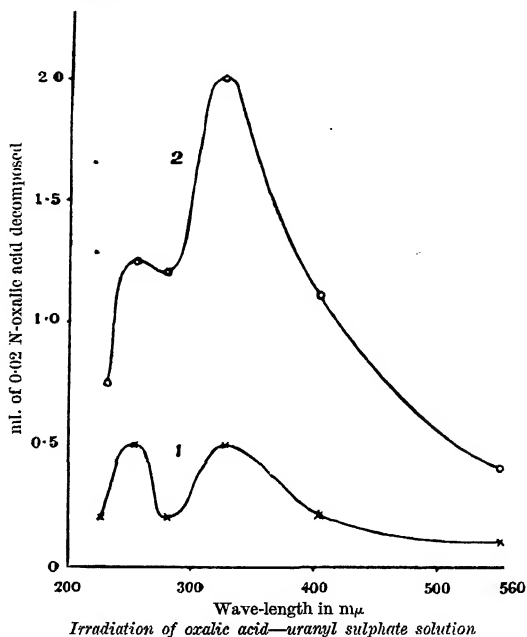
Irradiation of oxalic acid—uranyl sulphate solution

FIG. 54 (VI *)

circular section. The exposed portion was 6·5 cm. long and 1 cm. in diameter. Six of these, side by side, covered the spectrum from 600 $\mu\mu$ to 200 $\mu\mu$.

The spectrum of the mercury arc was photographed on Wellington Anti-Screen backed plates, with the slit adjusted to be as narrow as possible (about 0·05 mm.). A scale of wave-lengths prepared from these photographs was fixed in position on the instrument to coincide with the lines on a zinc sulphide fluorescent screen as recorded in the original paper, i.e. in 10^{-6} mm. In Chapter VII* on spectrometers results are given as 10^{-10} metres.

In this way the test tubes were placed in definite spectral zones. Those selected were as follows : (1) 650–450 $\mu\mu$; (2) 450–350 $\mu\mu$; (3) 350–300 $\mu\mu$; (4) 300–265 $\mu\mu$; (5) 265–240 $\mu\mu$; (6) 240–220 $\mu\mu$. These zones could be varied by a lateral displacement of the rack.

Exposures of duration varying from 1 to $2\frac{1}{2}$ hours were made with the test tubes, containing the solutions under examination, in the positions
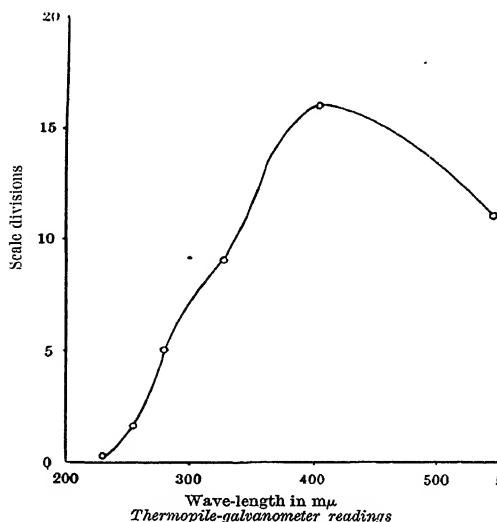

Wave-length in mμ
Thermopile-galvanometer readings
FIG. 55 (VI *)

indicated.   The intensities of the resulting reactions were plotted against wave-length with the results shown on the curves (Fig. 54 (VI *)).
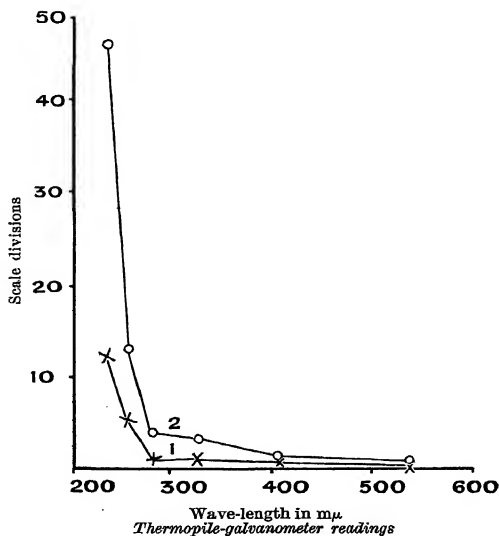

Wave-length in mμ
Thermopile-galvanometer readings
FIG. 56 (VI *)

With a view to reducing these curves to a uniform energy level, the radiation intensities in the zones were compared by means of a thermopile

and galvanometer. The thermopile used was a Moll instrument of aperture equal to the diameter of the tubes. The glass window of the instrument was removed, and the junctions were screened from draughts with a heavy black focusing cloth. Readings were taken under the same conditions of slit width and current intensity that obtained in the exposures of the tubes.

Six readings were taken at intervals of about two minutes in each position. The zero of the galvanometer was checked before and after each series to eliminate the effect of re-radiation from the apparatus. The resulting energy curve is given in Fig. 55 (VI *). From this curve, factors for the different positions were deduced such that the transmission of energy should be equal in all regions. The reaction curves were corrected by the aid of these factors (Fig. 56 (VI *)).

The Photo-conductivity Effect. When light falls on certain materials, notably selenium, it changes the resistances of these materials to the passage of an electric current.

In the case of selenium, red light is most effective, but the response to light stimulation is not immediate and this time lag is a disadvantage in some of the practical applications of the phenomenon.

A cell making use of this property consists of a glass disc on which are fine lines of platinum film arranged in the manner of the plates of a condenser : the platinum lines are separated by lines of selenium film. When no light falls on the selenium its resistance is very high, and if the platinum lines are connected by a battery very little current flows. When light falls on the selenium its electrical resistance is reduced which causes it to allow the current to flow more readily. Selenium is affected by moisture so that it is necessary to enclose the cell in a glass capsule.

Its disadvantages are that it requires a battery for its operation ; it is not constant or permanent in behaviour, the same light conditions do not always produce the same change in conductivity and its characteristics alter with age. Temperature changes have a comparatively large effect, and as mentioned above it is slow in response to changes in the intensity of the light : it is also damaged by all but low light intensities.

Rectifier or Barrier-layer Cells. Adams and Day [1] found that when a selenium rod was connected to platinum electrodes small self-generated currents were produced on exposure of either of the junctions to light.

Fritts [2] deposited a layer of selenium on a supporting metal, and on this was placed a film of gold so thin that light could pass through it to fall on the selenium, the gold film acting as one electrode and the metal plate as the other. The cell generated small currents when light fell on it.

A commercial cell of this type, the photronic cell, has now been perfected by the Weston Electrical Instrument Corporation to convert light energy into electrical energy of usable strength.

The maximum sensitivity ($\lambda = 5800$ Å) of this cell is in the neighbourhood of the maximum sensitivity of the human eye (5550 Å) but it is more sensitive than the eye to the infra-red and particularly is sensitive in the

[1] *Proc. Roy. Soc.*, 1876, *25*, 113.
[2] *Proc. Amer. Ass. for Adv. of Sci.*, 1883, *33*, 97.

ultra-violet region (for use in this region a quartz window is necessary instead of the usual glass one).

Since the distance between the anode and the back plate of the cell which acts as cathode is only a fraction of a millimetre, the resistance is comparatively low. The new cells appear to be very permanent; for example, they have been exposed to daylight continuously for periods up to 500 days without change in their characteristics, although when full sunlight was falling on them the self-generated current reached values as high as 10 milliamperes per cell.

The relation between the current and the number of lumens of light falling on the cell depends on the external resistance : when this is low, for example 3 ohms, the relation is practically a straight line and one lumen gives about 120 microamperes. The internal resistance of the cell appears to be in parallel with the external resistance and of course this internal resistance is decreased by the incidence of light in the case of selenium.

When an intermittent beam of light is used the cell behaves as though a condenser were connected across the internal resistance : when the frequency is not greater than 60 cycles the response of the cell is satisfactory, but with greater frequencies the response diminishes.

For low intensities the E.M.F. generated is about 7 millivolts per foot-candle. When more than one cell is to be used in order to increase the current output, the cells are connected in parallel, since when in series the increase in the resistance in the circuit is about the same as the increase in the E.M.F. so that the current is not increased. The temperature effect on the current is negligible when the external resistance is below 200 ohms. The cells experience a kind of fatigue in that when exposed to a constant source of light the current gradually falls for several minutes, so that for very accurate work it is necessary to wait a few minutes before taking a reading. The response to changes in intensity is however practically instantaneous, so that the passage of a rifle bullet through a beam of light can be recorded.

Photophysical and Photochemical Processes. The photoelectric effect and related phenomena may be stated more generally than in the form given at the beginning of this section.

When light rays, and especially high-frequency rays as well as X-rays and γ-rays, fall on an electropositive body (e.g. an alkaline metal), two effects are produced. (1) There is an increase in the thermal energy of the system, and (2) electrons are given off from the surface of the metal. The light is absorbed by the metal and the energy of certain electrons is so increased that some are ejected. This is the so-called photoelectric effect.

If the light absorbed by a substance (e.g. Barium platinocyanide) does not give sufficient energy to cast off an electron it may, however, raise it to a higher energy level and then return to the original state with emission of energy in the form of light. When the re-emission of energy is instantaneous it is known as *fluorescence*. (For contrast with *Raman effect*, see p. 316.) When it happens only after a certain time interval the phenomenon is known as *phosphorescence*. The slow combustion in air of certain substances (e.g. phosphorus) sometimes produce light effects. This phenomenon

may be classified as *chemical phosphorescence*, and is closely related to *chemiluminescence* (see later).

The photoelectric effect, fluorescence and phosphorescence may be grouped under the heading of photophysical processes. When a chemical change is involved in the absorption or emission it is classified as *photochemical*. One example of photochemical reaction is considered above in the measurement of the efficiency of ultra-violet light sources. There are, however, a number of other types of photochemical changes.

The reverse process is also known. There are a number of organic and biological reactions in which light is emitted during the reaction (e.g. oxidation of *o*-aminophthalic cyclic hydrazine). This phenomenon is known as *Chemiluminescence*.

In the Supplementary volume sections will be included on photophysical processes including fluorescence, phosphorescence, photochemical processes and chemiluminescence.

CHAPTER VII *

SPECTROMETRY

SECTION 1: THE SPECTROSCOPE

THE Spectrometer. The essential elements of a simple spectrometer consist of a collimator for producing a beam of parallel light, a rotatable level table to support the prism or diffraction grating, and a telescope for viewing the spectrum, mounted so that it can be rotated about the same axis as that about which the prism table rotates. To the telescope is attached a means for reading its angular position. The arrangement is shown diagrammatically in Figs. 1 (VII *) and 2 (VII *), which are respectively an elevation and plan in which A is the collimator, B the rotatable table, and C the telescope. At the end of the collimator A is a vertical slit D between two metal jaws; these jaws are bevelled, the metal being cut away on the inside (to avoid reflection). One jaw is usually fixed and the other, E, is movable by means of a finely threaded screw F so that the width of the slit can be varied. In a better arrangement both jaws are movable by the same screw so that the centre of the slit is always in the same position. A fine sharp slit with edges exactly parallel is very necessary, so that the jaws should be made of an incorrodible alloy such as platinoid or stainless steel, and should be treated with great care; they should never be closed too tightly for fear of injuring the knife-edges and should only be cleaned with the short wooden sticks supplied by the makers. G is a small glass prism which covers the lower half of the height of the slit. A source of light placed end-on to the collimator sends light through the upper half of the slit, while light from a second source at the side is totally reflected by the small prism into the lower half of the slit; in this way two spectra are obtained, one above the other, so that they can readily be compared. The prism can be turned aside when not in use. The tube carrying the slit is movable by means of the rack and the pinion attached to H. At K is the lens system of the collimator. This consists of a pair of lenses, adjusted for achromatism for the C and F rays; it is therefore, strictly speaking, not achromatic for other rays, but when the two glasses are suitably chosen, the departure from achromatism is very small. The focal length of this combination is equal to the length of the collimator, so that when the slit is illuminated, the beam which spreads out therefrom is rendered parallel by passing through the lens K. The telescope lens M is a similar combination. The eyepiece O is a Ramsden eyepiece consisting of two plano-convex lenses P and Q, of equal focal lengths; for achromatism the lenses should be a distance apart equal to the focal length, but every defect in the inner lens then becomes visible, so that it is usual to set the

lens at a distance apart equal to two-thirds of the focal length. In the tube T is fixed an index; this usually consists of two spider webs fixed in an X form with an angle of 60° between the legs. A metal pointer
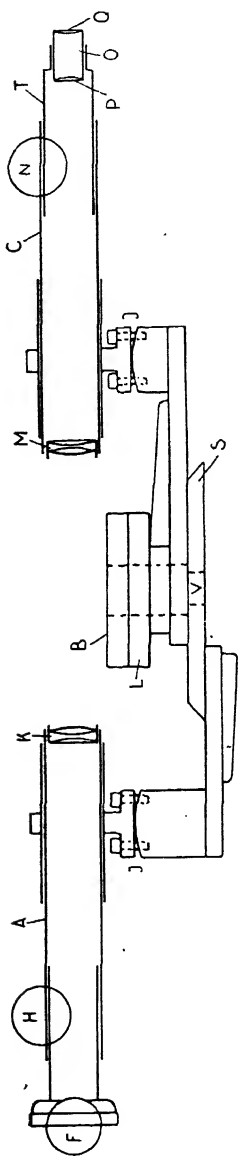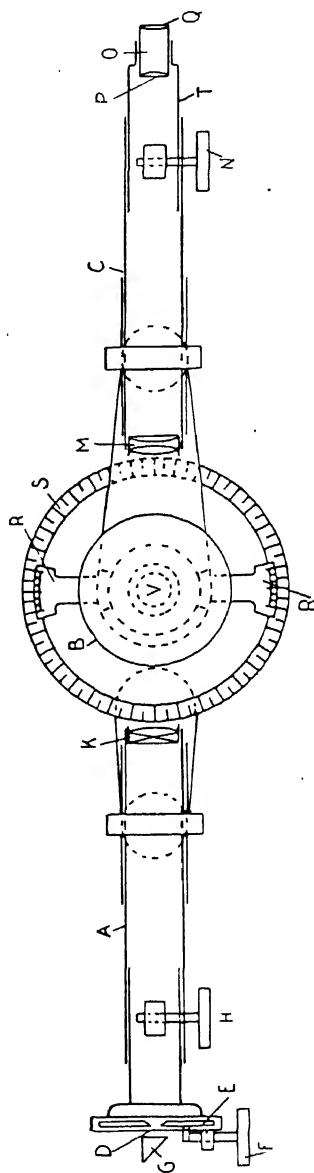

FIG. 1 (VII *)   FIG. 2 (VII *)

illuminated by a mirror from outside is sometimes used and is convenient when examining lines against a dark background. In some instruments lateral dark slides are provided which can be used to cut out bright lines when examining faint ones.

In the micrometer eyepiece, in addition to fixed vertical webs, there is a single web movable across the field by means of a micrometer screw. By this means the distance between two spectrum lines can be measured in terms of the divisions of the head of the micrometer drum. The eyepiece is movable in the tube T so that it can be focused on the index, and the tube T is movable by means of the rack and the pinion N so that the telescope can be focused for parallel light.

The prism table B rotates about the central pin V; B and L (which is fixed) are both graduated on their edges. The telescope arm is also free to move round the pin V, and this arm carries the two verniers R R which move over the graduated scale S. The telescope and the collimator can be adjusted so that their axes are horizontal, by means of the blocks and nuts J. The telescope arm can be clamped to the stand and then be given a slow motion by means of a micrometer screw (not shown). This instrument is not adapted to measurements of greater precision than 30' of arc. In more accurate forms of instrument, the collimator is mounted more rigidly and on the base plate; the telescope is also more rigidly mounted and provided with a counterpoise for its weight. Simple verniers are replaced by either two or four micrometer microscopes reading directly to half-seconds and the graduated scale has a diameter of 12 to 15 inches. If the micrometer microscopes are all attached to a ring which can be moved round the axis and clamped in any position, all errors due to defective centering can be eliminated.

The Prism. As a compromise between maximum sensitivity and maximum definition we are led to decide in favour of a 60° prism. If all three faces are polished this gives us the further advantage that measurements can be made with each angle in turn. If the edges of the prism are parallel and the angles do not greatly deviate from 60°, the mean of the deviations when each angle is used in turn is equal to the deviation with a prism of exactly 60° angle, so that the measurement of this angle is obviated.

Adjustment of the Spectrometer. First the eyepiece is focused on the cross-wires and then the telescope is focused for parallel rays by directing it at some object 200 or 300 yards away, such as telegraph wires or slates on the roof of a building; the focusing is done by moving the tube T by means of the rack and pinion N and its correctness can be tested by seeing that there is no parallax between the image and the cross-wires, i.e. that on moving the eye from side to side they do not appear to move relatively to one another, so that the focus on the cross-wires is not disturbed. The telescope is then directed towards the collimator, the slit of which is illuminated with sodium light, and the tube with the slit attached is moved by means of the rack and pinion H until the edges of the slit are clearly in focus: here again the accuracy of the setting can be tested by the parallax method. Since the telescope was originally focused for parallel light and the slit is now in focus, the collimator has been adjusted to give a parallel beam of light. As tests for the exactness of the setting, Lippmann used two pieces of plane-parallel plate glass placed one above the other and inclined to one another at an angle; these are placed on the prism table and the slit is illuminated with sodium light; the upper half of the beam

passes through the upper plate, the lower half of the beam through the lower plate, and if the collimator has been adjusted so that the beam is parallel, no displacement of the two halves of the image will be produced by the two plates. Another method consists in using a prism. This is first set in the position of minimum deviation; the telescope is then moved a little to the side, so that on turning the prism in either direction the line is brought on to the cross-wires. If the adjustment is correct the fine line will appear to be focused equally well whether the prism is turned one way or the other. If one image appears better than the other the adjustment is made as follows : Calling the two positions of the prism A and B—with the prism at A the telescope is focused sharply on the line, the prism is then turned to B and the collimator adjusted so as to give a sharp image, the prism is turned back to A and the telescope again focused and the process continued till the focusing appears equally good in either position.

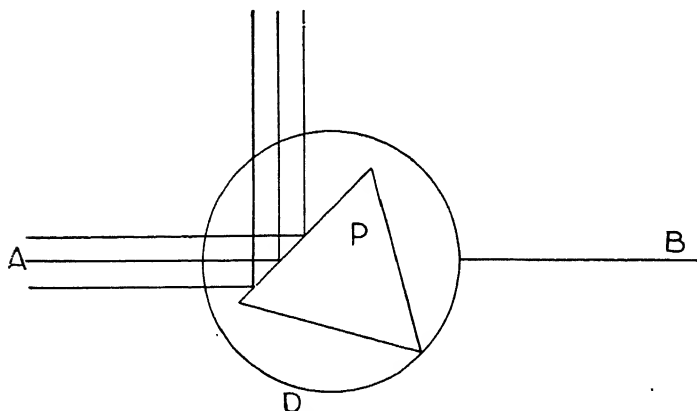The next step is to adjust the optic axes of the telescope and the colli-

FIG. 3 (VII *)

mator so that they are perpendicular to the axis of rotation of the telescope. The centre of the slit on the collimator is marked. Some instruments are provided with a slide which moves over the slit and has a wedge-shaped opening, but in case this is absent two parallel fibres are fixed horizontally one on either side of the centre and about 0·5 to 1 mm. apart. A prism P is placed on the table (Fig. 3 (VII *)) with one face inclined at 45° to the collimator axis. The telescope is moved round to position A so that the slit can be observed by reflection in the face of the prism. The prism table is then levelled so that the centre of the slit coincides with the centre of the cross-wires. The telescope is moved to B and an auxiliary telescope, focused for parallel rays, is put at A so that the slit can be seen; this telescope is then adjusted by means of its own levelling screws so that the image of the centre of the slit coincides with the intersection of its cross-wires. The axis of the auxiliary telescope now occupies exactly the same position as that previously occupied by the axis of the spectroscope tele-scope. The prism is removed, a light is placed behind the eyepiece of the auxiliary telescope to illuminate its cross-wires, and these are then observed

through the spectroscope telescope at B : the centres of the cross-lines should appear to coincide. If they do not the telescope is adjusted till the error is reduced to one-half, the telescope is then moved to D and the level of the collimator is adjusted to bring the centre of the slit on the cross-wires. The accuracy of this adjustment should be tested by repeating the whole process. In Fig. 4 (VII *) is shown an auto-collimating eyepiece by Abbe. A glass prism has an angle of 45° as shown at b ; in Fig. 4 (VII *) a this prism is shown fixed at d, behind the second eyepiece lens, with the edge in the same plane as the cross-wires e. · If a lamp is placed above d the light is totally reflected by the 45° face and passes out of the prism to the right, thus giving a bright background to the top end of the cross-wires. If the telescope is now placed opposite a vertical glass plane surface the image of the tops of the cross-wires against the bright background will be reflected back into the telescope, giving the appearance shown in Fig. 5 (VII *), where f is quite black because all the direct light is
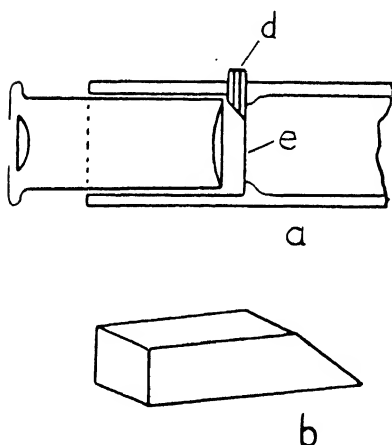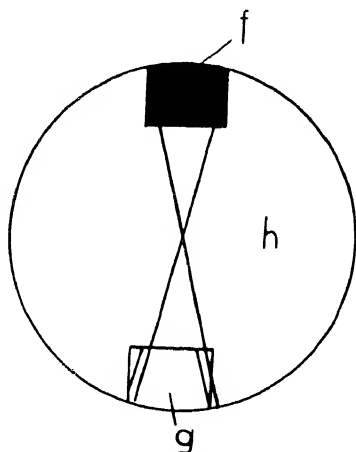

FIG. 4 (VII *)   FIG. 5 (VII *)

cut out by the prism d ; g is bright and is crossed by the two dark lines which are the images of the cross-wires, and the field h is fairly dark and is crossed by the cross-wires. The setting shown in the diagram is the appearance when the axis of the telescope is horizontal but not exactly perpendicular to the plane of the sheet of glass ; if the telescope is moved round slightly, the cross-wires and their image will coincide ; if the axis of the telescope is not horizontal the image lines will both be either inside or outside the cross-wires. To use the auto-collimating eyepiece to adjust the spectrometer, a parallel-sided piece of plane glass is placed on the prism table and the image is viewed through the telescope ; the prism table is then adjusted until the correct appearance is seen, the telescope is next turned through 180°, and the opposite side of the sheet of glass is viewed. The appearance will be exactly the same as before only if the axis of the telescope is perpendicular to the axis of rotation ; if this is not so, half the deviation is corrected by inclining the telescope and half by inclining the glass sheet, and the test is again repeated, and so on until the correct result

is obtained. A similar test can be applied without the aid of an auto-collimating eye-piece provided that the glass plate is silvered on both sides. The telescope, having been correctly adjusted, is brought opposite the collimator and this is then adjusted till the centre of the slit is in line with the intersection of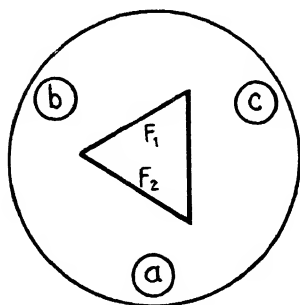 the cross-wires. The next step is to test the level of the prism table. If F_1 and F_2 are the faces to be used, the prism is set on the table as shown in Fig. 6 (VII *) with the face F_1 perpendicular to the line joining the two levelling screws ab. The telescope is fixed in any convenient position and the prism table rotated until the image of the slit, seen by reflection in face F_1, is on the cross-wires. The table is then levelled by means of the screw a until the centre of the slit is on the cross-wires; the table is next rotated till F_2 occupies the position previously taken by F_1, and the centre of the image is adjusted by the screw c.

FIG. 6 (VII *)

The position of the source of light is adjusted so that the aperture of the collimator is evenly filled with light ;. the source is placed at a distance from the slit and its position is adjusted until the rectangular patch of light is centrally disposed in the collimator lens ; a lens is interposed between the source and the slit so as to form an image on this, the focal length and aperture of the lens being chosen so that the cone of light just fills the collimator lens.

Measurement of the Angle of the Prism. In the first method the refracting edge of the prism is placed over the centre of the table with the base approximately perpendicular to the collimator axis ; the telescope is
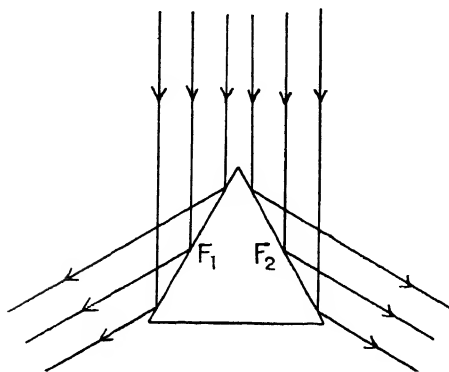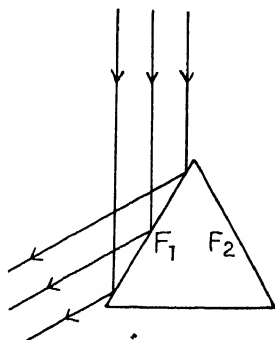

FIG. 7 (VII *)

FIG. 8 (VII *)

then moved so that the slit image is focused on the cross-wires by reflection in face F_1, and then by reflection in face F_2 ; the angle between the two positions of the telescope is then twice the angle of the prism. This arrangement is shown in Fig. 7 (VII *), where it will be seen that the image produced

on one side is by a different part of the beam from the collimator from that giving rise to the image on the other side; this reduces the accuracy of the method. In the second method the prism is placed as shown in Fig. 7 (VII *), the telescope is adjusted till the image of the slit is on the cross-wires, and the reading of the prism table is taken; the table is then rotated until the image produced by the reflection in F_2 is in focus and the reading of the table is again taken. The angle of the prism is then 180° minus the angle through which the table has been moved.

When an auto-collimating eyepiece is available an excellent method consists in adjusting the telescope so that it is perpendicular first to face F_1 and then to face F_2. The angle of the prism is then given by 180° minus the angle through which the telescope moves.

Measurement of Refractive Index by the Minimum Deviation Method. The prism must be placed on the table in such a way that the bisector of the refracting angle is over the axis of rotation and also that it employs the apertures of the collimator and the telescope centrally. This result is not attained when the centre of the prism is over the centre of rotation, but when that lies behind this, i.e. the prism is moved towards its base. The eyepiece of the telescope is viewed with a magnifier; the illuminated aperture of the prism will then be seen with the aperture of the telescope, and the prism can be moved until the former is symmetrically disposed in the latter, care being taken that the bisector of the refracting angle remains over the centre of rotation. The measurement for any particular line can then be made. Suppose it is the D line. The prism table is rotated and the movement is followed with the telescope; if this is on the left of the line of the collimator axis, the image will be found to move up to the right and then back towards the left. The extreme position of the image on the right is found and the telescope is clamped, the final adjustment being made with the fine-adjustment screw so that when the table is turned the image just moves up to the cross-wires. The prism table is now rotated so that the refracting edge is to the left, the telescope must therefore be turned over to the right and a new setting made on this side. The angle through which the telescope is turned is twice the angle of minimum deviation. The method obviates the necessity of observing the zero reading with telescope and collimator in line, a reading which cannot be made with great exactness. The refractive index is given by the equation

$$\mu = \frac{\sin \frac{1}{2}(\delta + \varphi)}{\sin \frac{1}{2}\varphi}$$

where δ is the angle of minimum deviation and φ is the refracting angle of the prism.

When the lines which are being measured are not packed very closely together, much better settings can be obtained by using instead of the narrow slit a broad one with a spider web down its centre; the image seen then consists of a dark shadow on a broad bright background and the cross-wires can be set on this with great ease. The vertical line may be obtained by mounting a fibre of quartz or glass on a metal washer, and cementing a microscope cover-slip on for protection; the device can then be fixed in front of the slit with wax.

Measurements of Wave-length with the Prism Spectrometer.
The more important standard lines used are :

		Wave-length in 10^{-10} metres			Collie tube	
Cadmium		4799·9	blue	Helium	7065·5	r
		5085·8	green	Helium	6678·4	r
		6438·5	red	Hydrogen	6563·0	r
Mercury		5168	g	Mercury	6152·0	
		5173	g	Helium	5875·9	y
		5184	g	Mercury	5790·5	y
		5529	yellow	Mercury	5767·5	y
Sodium	D_2	5890·0	orange	Mercury	5461·0	g
	D_1	5895·9	o	Helium	5015·7	g
Hydrogen		4102	violet	Helium	4922·0	g
		4340	b	Hydrogen	4861·5	b
	F	4861	g b	Helium	4713·3	b
	C	6563	r	Helium	4471·6	v
Helium		3188	v	Mercury	4358·6	v
		3889	v	Hydrogen	4340·7	v
		4471·5	b			
	D_3	5875·6	v			

Improved figures are given by Köstees.[1]

The wave-lengths given in the first column are for the brightest lines only of the elements ; those in the second column are for the Collie tube, which contains a mixture of helium and hydrogen with a trace of mercury vapour. A calibration curve has first to be constructed for the spectrometer ; this is done by finding the minimum-deviation position for each line and plotting on squared paper the deviation against either the wave-length or the oscillation frequency. The oscillation frequency is the reciprocal of the wave-length reduced to vacuum. To reduce the wave-length of a line measured in air to its value *in vacuo*, it must be multiplied by the refractive index of air for light of that particular wave-length. The refractive index for air at 0° and 760 mm. is given by the equation

$$10^7 \, (\mu - 1) = 2878 \cdot 7 + 13 \cdot 16 \lambda^{-2} + 0 \cdot 316 \lambda^{-4}$$

where λ is measured in 10^{-6} metres. The correction is most simply applied by making a small addition to the wave-length observed ; the correction ranges from $2 \cdot 52 \times 10^{-10}$ metres for $\lambda = 8,000$ to $0 \cdot 70 \times 10^{-10}$ for $\lambda = 2,000$. The advantage of plotting against oscillation frequency is that a much flatter curve is obtained. Once the curve has been determined the wave-length of an unknown line can be read off as soon as a determination of the angle of minimum deviation has been obtained for that line. The wave-length in the visible spectrum varies from approximately 3,900 Å to 7600 Å. For long waves in the infra red however μ is often taken as the unit [2] so that λ 12,500 Å is indicated as 1·25 μ. The spectrum of an element is often a precise and accurate test for minute quantities. It is specially important in the case of the elements of the argon group where no chemical compounds exist for comparison. The accurate estimation of Krypton and Xenon by the spectroscope is described by Mourlau and Lepape.[3] The

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[1] *Phys. Zeits.*, 1934. [2] Fowler, *Report on Series in Line Spectra*, 1922, 1.
[3] *Compt. rend.*, 1911, *153*, 740 ; 1922, *174*, 908.

method depended on the comparison of Krypton and Xenon lines with prominent well defined argon lines. The formulae now used are due to Meggees and Peters.[1]

Sources of Light. (1) *Flame Spectra.* When the substance can be brought into solution the device shown in Fig. 9 (VII *) can be used ; the tube contains the solution, to which ammonium acetate has been added to facilitate creeping along the ' wick ', which consists of a few platinum wires extending into the flame of a Meker burner. Another device is shown in Fig. 10 (VII *), where *a* is the tube of a porcelain Bunsen burner, *d* is a strip of asbestos paper wired on with platinum wire, *b* is a piece of glass tubing,
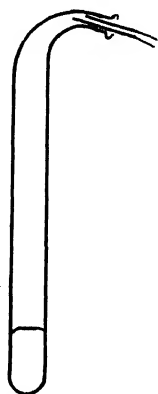

FIG. 9 (VII *)   FIG. 10 (VII *)
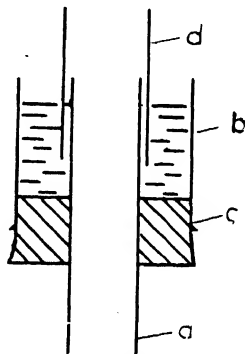
and *c* a rubber stopper. The solution is placed in the space between *a* and *b*. Solid substances can be held in small silica spoons.

(2) *Arc spectra.* When the metal is not too easily fusible, rods of the metal may be used for both the poles of the arc or the negative may be of the metal and the positive of carbon. Another excellent way of obtaining the required spectrum is to use cored carbon rods, i.e. rods of gas carbon having a central core of the substance under examination. Still another way is to put small pieces of the substance in the crater of the positive pole of a carbon rod ; the last method, though simple, gives an unsteady arc.

Spark Spectra. In this case sparks from an induction coil are passed between wires of the metal. The best results are obtained when a condenser is connected across the spark-gap ; the capacity of the condenser being so chosen that a spark of 2 to 3 mm. can be obtained with iron electrodes in air. Sparks may also be passed between a platinum wire and a solution of a salt of the metal to be examined. Some forms of apparatus for this purpose are shown in Figs. 11 (VII *), 12 (VII *) and 13 (VII *). In the first a piece of capillary glass tube draws the liquid up round the lower wire. In the second the electrodes are wedges of graphite with their edges parallel to the slit ; the current is led in by the platinum wires, which are wound round the graphite and the glass tube ; the grooves between the fibres of the graphite serve to lead up the liquid by capillarity. In the third a piece of gold-wire passes right through the capillary to the top of the

[1] *Bull. U.S. Bur. Stand.,* 1918, *14,* 697.

lower cup ; here it is surrounded by a small piece of capillary   tube which serves to keep the end always moist.
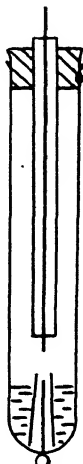

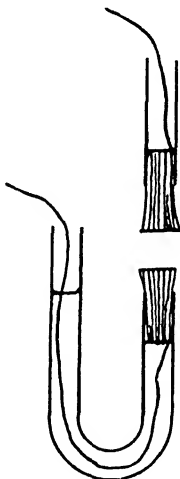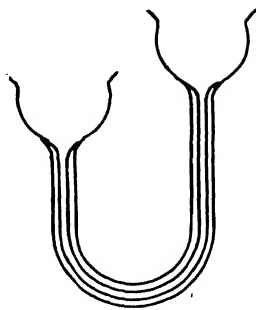FIG. 11 (VII *)   FIG. 12 (VII *)   FIG. 13 (VII *)

Spectra of Gases. Two convenient forms of apparatus are shown in Figs. 14 (VII *) and 15 (VII *), the H form and the Goetze ; both of these are of the end-on form, in which the discharge has to pass through a long
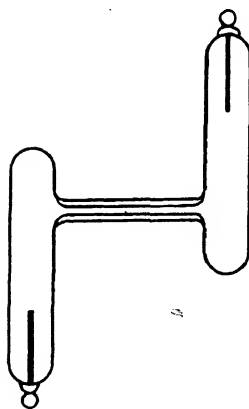

FIG. 14 (VII *)   FIG. 15 (VII *)
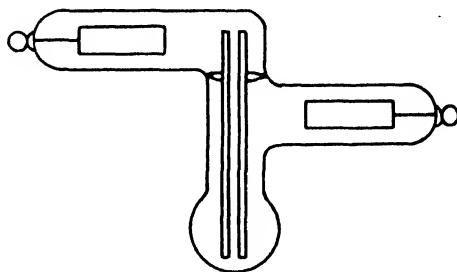
straight tube, so that when placed in the end-on position to the slit, a source of considerable intensity is obtained. Tubes of the H form and also straight tubes can be obtained with taps so that any desired gas can be introduced for examination. An induction coil is used to excite the gas.

The Direct-vision Spectroscope. For many chemical purposes, when accurate measurements are not essential, the direct-vision spectroscope shown diagrammatically in Fig. 16 (VII *) is useful. Here a is an adjustable slit and b the collimator lens system ; c and e are crown-glass prisms

cemented with Canada balsam to the dense flint-glass prism *d*, thus producing dispersion of the light with very little deviation; the lens *f* and the eyepiece *g* form the telescope, which in some cases is provided with cross-wires or a pointer; the telescope is pivoted at its forward end and can be moved laterally by means of the screw *k* working against the spring *l*
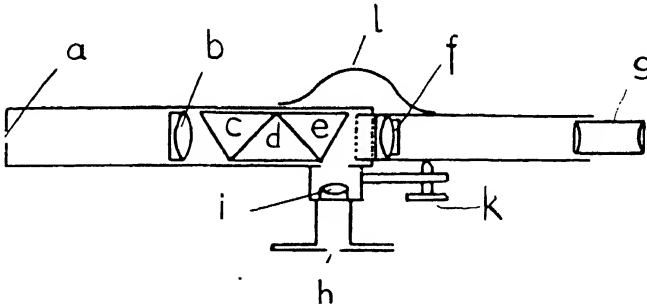
FIG. 16 (VII *)

so as to bring any particular line on to the cross-wires. In some forms the head of the screw *k* is graduated in order to enable the position of a line to be recorded. In other forms a graduated scale at *h* is illuminated, the light rendered parallel by the lens *i* and then reflected from the face of the prism *e* into the telescope, when it is brought to a focus in the same plane as are the spectrum lines.

FIG. 17 (VII *)

The Constant-deviation Spectroscope. This instrument is shown diagrammatically in Fig. 17 (VII *). The prism (Fig. 18 (VII *)) is a

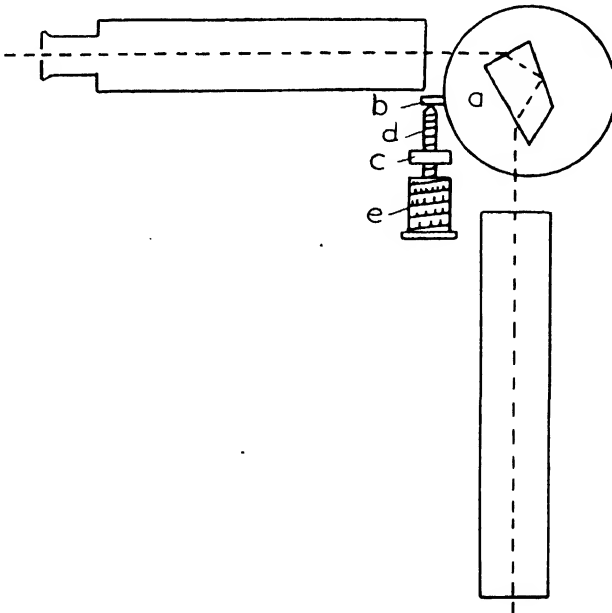single block of glass which can be regarded as being built up of three prisms, two of 30° with a third of 45° between them. When a ray of light *ab* is incident on the face of AB so that it is refracted along *bc* parallel to BC, it is totally reflected at the face DC so that the reflected ray *cd* is parallel to AC ; the angle of incidence of *cd* on AD is then equal to the angle of refraction which *bc* makes with AB ; it therefore emerges from AD along the path *de* in a direction which is perpendicular to the original direction *ab*. ABC and ADF may be looked upon as two halves of a 60° prism and in each case the ray is parallel to the base ; that is, it is in the minimum-deviation position.

In order that the ray *bc* shall be parallel to the line BC, the angle of incidence must be chosen suitably ; thus, with blue light of short wave-length, the refractive index is high, so that the angle of incidence must be large ; with red light it will be smaller. Means are therefore provided for rotating the prism, so that while both collimator and telescope are fixed at right angles, the angle of incidence of the light in the prism face is varied by turning the latter. The arm *b* in

FIG. 18 (VII *)

Fig. 17 (VII *) is fixed to the rotatable table *a* ; the screw *d* turns in the nut *c* which is fixed to the frame, and the hardened point of this screw presses against *b*, which in turn presses against a spring not shown in the diagram. By turning the screw *d*, *b* is pressed forward and the table *a* rotated. Attached to the head of the screw *d* is a drum *e* in which is cut a spiral slot; a pointer has a projection which fits into the slot so that when the drum is turned, the pointer, which slides between guides attached to the frame, moves forward along the drum parallel to the axis of 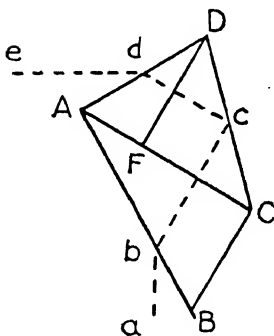the screw. The spiral on the drum is graduated to read wave-lengths directly. In using the instrument the prism is clamped into position and the slit is illuminated with light of known wave-length λ, the drum *e* is turned until the pointer points to the scale reading λ, and the cross-wires in the eyepiece are moved laterally until they coincide with the image of the line. In the Hilger instrument focusing is done by turning a milled ring which moves the object glass, the eyepiece remaining fixed. The instrument has the advantage of not requiring separate setting for each line in the minimum-deviation position, and of reading wave-lengths directly with an accuracy of 1Å.

The microspectroscope (Sorby-Browning) shown in Fig. 19 (VII *) is extremely useful in the examination of small quantities of coloured sub-stances, as for example in measuring the absorption bands of blood. The instrument replaces the eyepiece of an ordinary microscope. At *a* is a slit adjustable by means of the milled screw *b*. Above the slit is a small direct-vision spectroscope which can be focused by means of the milled head shown in broken line at *d*. Light from an adjustable mirror *m* is reflected into the tube *h*, and illuminates the micrometer scale *l* ; the scale is reflected by means of the half-silvered glass shown at *f* and is focused by means of the lens *g*, which can be moved by the milled head shown in dotted line.

At c is a total reflection prism which covers half the slit so that light from a solution in a tube outside the instrument can pass in through the aperture n and be compared with the substance on the table of the microscope. This prism can be moved aside when not required. As an example of the method of using the instrument the cyanhæmochromogen test for blood-stains may be described. Supposing the stain to be on a piece of cloth, a portion of the stain about half a centimetre in diameter is cut out and placed on a microscope slide and moistened with distilled water. After a few minutes one drop of a 10 per cent solution of potassium cyanide is added, when the blood will turn cherry red in colour. A drop of ammonium sulphide is added and a cover-slip placed over the cloth. The stain is then placed under the microscope and is illuminated with white light, and the microscope is focused on the brightest part of the stain. The ocular is removed and is replaced by the microspectroscope, when two dark bands will be seen in the green region of the spectrum. By means of the milled heads b and d the slit is adjusted and the bands are brought into focus. A comparison solution known to contain blood and treated with potassium cyanide and
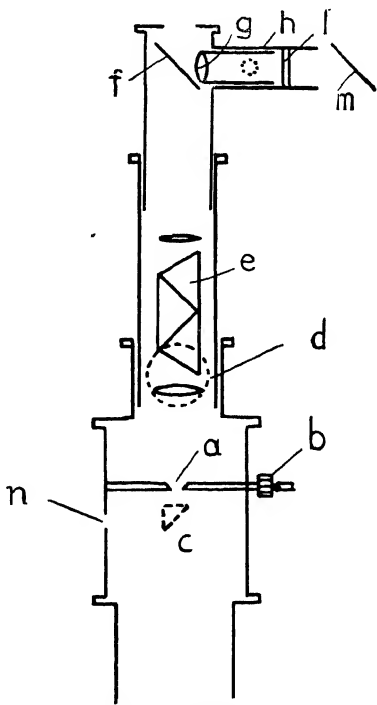

FIG. 19 (VII *)

ammonium sulphide can be placed in a test tube in the clips provided outside the aperture n, and this can be illuminated with white light so as to give bands for comparison ; or the scale l can be focused by the mirror m and the lens g so that the position of the lines can be read on the scale.

The Spectrograph. A photographic reproduction of a spectrum has several advantages over visual observation. The record is a permanent one, and in addition the photographic plate is sensitive in the ultra-violet region where the eye can no longer detect the lines. Owing to the absorption bands of glass in the more extended region it is usual to construct the prism and the optical parts of the apparatus of quartz. For the lenses an achromatic pair is desirable, and a very suitable combination is that of quartz and fluorite ; fluorite, however, is practically unprocurable, and the less satisfactory combination of quartz and calcite is used instead. Calcite unfortunately has an absorption band in the neighbourhood of $\lambda = 2,000$ Å. With this apparatus almost the whole spectrum can be brought into focus on a flat plate, the camera being slightly inclined to the axis of the telescope. Using quartz alone it has been found possible to cut the lenses and prisms in such a way that the focal curve is absolutely flat. In this case the plate has to be inclined at an angle of 27° with the telescope axis ; such an instru-

ment is made by Messrs. Hilger. With quartz optical parts cut in the ordinary way the focal curve is not flat, and films have to be used and are bent to the correct curve with the aid of a template fitted in the dark slide. The dark slide which carries the plate works up and down in vertical grooves by means of a rack and pinion at the side; a scale and index show the position of the plate, on which a number of exposures can be made, one above the other, and a known and unknown spectrum can be photographed in juxtaposition. Slow plates give better results than rapid ones and any good make will give good results in the blue and ultra-violet. For work in
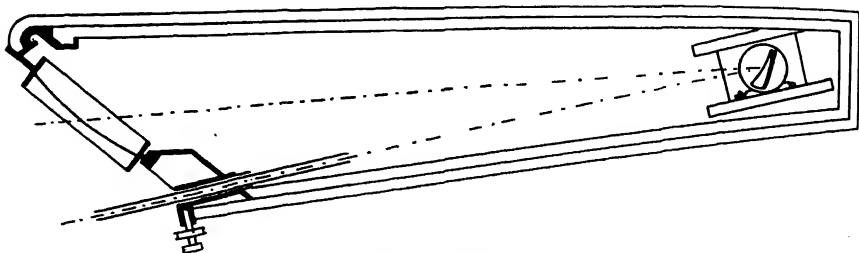

FIG. 20 (VII *)

the red region Allochrome are evenly sensitive to 5,600 Å, Panchromatic A are sensitive to 6,800 Å, Panchromatic B are sensitive to 7,800 Å. Plates are now available which after hypersensitizing are sensitive to as far as 12,000 Å in the infra-red.

The Féry spectrograph is of special interest in that the collimator and camera lens are dispensed with. The prism is a 30° quartz one with both the front and back surfaces curved, the latter being silvered so that the light traverses the prism in both directions, thus avoiding trouble due to rotatory properties in quartz. The theory of the prism is given in Baly's
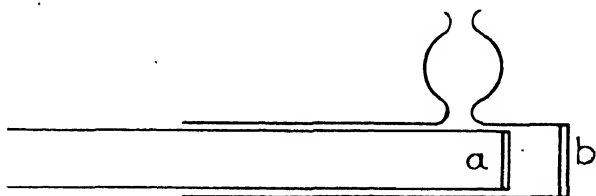
FIG. 21 (VII *)

Spectroscopy. With this instrument the spectrum is formed over a curved surface and the lines themselves are curved. The instrument is shown diagrammatically in Fig. 20 (VII *).

The photographic method is also of great value in the study of absorption spectra. The maximum absorption is not necessarily at the centre of the band, so that the usual procedure is to photograph the spectrum through layers of the liquid of gradually decreasing depth; the bands are then found to become narrower and narrower until they vanish. A suitable tube is that devised by Baly and shown in Fig. 21 (VII *). The two tubes are closed at the ends *a* and *b* and open at the other end. They are connected

together by means of a piece of wide rubber tubing so that the inner one can slide in the outer, enabling the thickness of liquid between *a* and *b* to be varied. The inside of the inner tube is lined with black paper to prevent the entrance of reflected light. The Baly tube can now be obtained (A. Hilger, Ltd., London) with the glass and quartz parts replaced by fused silica and the inner tube ground into the other tube. The grinding is so well done that there is no lateral shake. As an example, an N/10 solution may be prepared and the spectra photographed through layers 30, 25, 20, 15, 12, 10, 8, 6, 5, 4 mm. thick, a comparison spectrum being photographed on the same plate. If the last photograph still shows the bands, the series may be repeated with an N/100 solution. The wavelengths of the limits of the absorption band for each thickness of the solution are read off from the comparison spectrum and are converted into oscillation frequencies. These are then plotted as abscissae against the logarithms of the relative thicknesses of the solution, and the points so obtained are joined by a curve. As a source of light, the continuous spectrum is less satisfactory than one composed of a large number of lines closely packed together. Such a source can be obtained with an arc between carbon poles impregnated with the oxides of uranium and molybdenum. Carbon rods 1 cm. in diameter are used and their ends are filed to a wedge shape. The wedges are boiled in a uranium nitrate solution, dried and ignited. This is repeated three times with uranium nitrate solution and then three times with ammonium molybdate solution. An iron arc is also a very satisfactory source of light as it gives a large number of distinct lines spread over the spectra.[1]

A vacuum iron arc lamp without water cooling for spectroscopic purposes has been designed by Van der Zwall[2] (Fig. 22 (VII *)).

FIG. 22 (VII *)

It is an improvement on the vacuum iron arc lamp, in which the heat produced by the arc is carried off by means of water cooling. The main advantages of the new arc are that there is (1) no water cooling, (2) the electrodes can be easily interchanged, (3) no parts of the lamp house are under tension, (4) ignition and adjustment of the electrodes with the same knob, (5) the arc lamp burns in a vacuum of about 4 cm. of mercury (72 on the manometer scale) ; this vacuum can be maintained by means of a filter pump, (6) constant arc, suitable for continuous work, (7) the emitted light gives very fine spectral lines.

The lamp house consists of a bronze cylinder from which the holder of the electrodes is insulated. The electrodes are placed horizontally. A removable tube with quartz plate is fixed to the front wall. On the back wall are mounted a manometer for controlling the vacuum, a connecting piece for the rubber tubing and a valve for the regulation of the vacuum. The heavy stand of the lamp is adjustable vertically. At a current of about
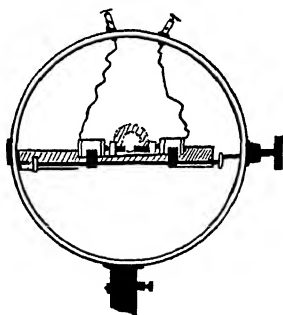
[1] Morgan and Reilly, *Trans. Chem. Soc.*, 1913, *103*, 1494.
[2] Made by P. J. Kipp & Zonen, Delft, Holland.

3·5 amps. the temperature of the lamp house does not become higher than about 70°. Using a suitable series-resistance, the lamp can be connected to direct tensions of 110–220 volts.

Spectrophotometry. The quantitative analysis of a solution which shows absorption bands can be carried out by two methods. In the first method a photograph is taken with a known thickness of the solution of unknown concentration. A series of photographs is also taken through solutions of known concentration and varying thickness. By comparison of the photograph of the absorption spectrum of the solution under test with the standard photographs the concentration of the former can be obtained. In the second method the beam of light is divided into two parts ; one of these suffers a reduction in intensity owing to the absorption by the solution, and the intensity of the other is reduced to the same value by some device which enables the reduction to be measured. The quality of the two reduced beams can be compared photographically, but it is more usual to make a visual comparison. The instrument used is called a spectrophotometer.

If I_0 is the initial intensity of the light and I is the intensity after transmission, $I = I_0 e^{-kt}$, when k is a constant and t is the thickness of the absorbing layer : hence $I = I_0 a^t$; a is called the absorption coefficient and is equal to the fraction of the light transmitted by a layer 1 cm. thick. The extinction coefficient is defined as the reciprocal of the thickness which reduces the intensity of the light to one-tenth. Let this be denoted by α.

$$\text{Then } \frac{I}{I_0} = \frac{1}{10} = e^{-kt} = a^t.$$

$$\text{Here } t = \tfrac{1}{\alpha}$$
$$\therefore a^{\frac{1}{\alpha}} = 10^{-1}$$
$$a = 10^{-\alpha}$$
$$\therefore I = I_0\, 10^{-\alpha t}$$
$$\text{and if } I_0 = 1$$
$$-\log I = \alpha t.$$

As an example, if $t = 20$ mm. and
$$I = \tfrac{3}{4} I_0.$$
$$-\log \tfrac{3}{4} = \alpha \times 2$$
$$\log 4 - \log 3 = 2\alpha$$
$$0·6021 - 0·4771 = 2\alpha$$
$$0·1250 = 2\alpha$$
$$\alpha = 0·0625.$$

The absorption ratio of a substance in a given solvent is defined as the ratio of the concentration to the extinction coefficient. This is a constant and can be determined once for all. Denoting the absorption ratio by A, we have $A = \dfrac{c}{\alpha}$; hence, knowing A and making a determination of the extinction coefficient α, we can determine the concentration c.

In the Hüfner spectrophotometer the spectroscope is a constant-deviation instrument provided with a drum giving wave-length readings. A Pointolite lamp makes a convenient source of light. The cell in which the solution is placed is called a Schulz cell. This is a rectangular glass cell 11 mm.

broad and having on the base a rectangular block made of the same glass, 10 mm. broad and half as high as the cell: thus a cavity 1 mm. broad is left between the block and the cell. The upper half of the beam passes through 11 mm. of solution, the lower half through 1 mm., and the conditions of loss of light due to reflection at the various surfaces are the same for each. The cell can be raised and lowered on a stand. The light now enters the tube of the collimator and the lower beam passes through a Nicol prism which polarizes the light perpendicularly and also reduces its intensity. The two beams next pass through an Albrecht rhomb, which is made of the same glass as the dispersing prism and is cut so that the angle of incidence of light on the face of the rhomb is the same as the angle of incidence on the face of the prism. By this means the polarization produced by the rhomb and the prism are balanced out. The rhomb brings the two beams into close juxtaposition on the slit of the collimator with a sharp dividing line between them. The light is collimated, dispersed by the prism, and then enters the telescope. Both parts of the beam pass through a second Nicol prism which can be rotated and the angle of rotation measured, and are brought to a focus and are observed with an eyepiece provided with a shutter on each side; these can be pushed in and out so as to isolate any desired part of the spectrum. On looking through the eyepiece two spectra are seen, one above the other, with a sharp dividing line between them. In making a measurement, allowance has first to be made for the reduction in intensity of the lower beam by its passage through the first Nicol prism. The analysing nicol is set at zero and a wedge of neutral-tinted glass is mounted so as to cover the upper half of the slit; this wedge is moved laterally until the intensity of the two spectra appears to be the same. The solution is placed in the Schulz cell and the spectra will be found to match no longer; by means of the wave-length drum that portion of the spectrum in which measurements are to be made is brought into the field of view, and by moving the shutters in the eyepiece the lateral parts of the spectra are cut out. The unabsorbed beam is now of course bright, but it is polarized, while the absorbed beam is not. On rotating the analyser the intensity of the first beam is reduced, while that of the second is unaffected. The analyser is turned until the intensities of the two spectra match, and the angle θ through which it has been turned is read off by means of a vernier and circular scale. Then $I/I_0 = \cos^2 \theta$. An attachment which can be used to convert a quartz spectrograph into a spectrophotometer for work in the ultra-violet is shown in Fig. 23 (VII *). The light from the source L passes along two paths. In the upper path it passes through the rotating sector S, which has a variable aperture, then through the quartz wedge prism P, the lower half of the quartz bi-prism B, which deviates it so that it passes into the collimator and parallel to the axis thereof. The other beam passes through the cell A, which has quartz ends and is intended to contain the absorbing liquid; then through the rotating sector S', of fixed aperture, through the wedge prism P' to the upper half of the bi-prism in B, which deviates it into the spectrograph. Thus two spectra are obtained, one above the other. The intensity of the light in one beam is lowered by the absorption in A, that in the other by decreasing the area of the sector opening. For ultra-violet work a series of photographs is taken of the pairs of spectra

obtained when the area of the sector S is altered step by step. On com-
parison of the two spectra of a pair it will be seen that while one is reduced
in intensity throughout, the other is reduced at certain points only, these
points being the absorption bands ; if any particular point of the spectrum
is taken, that pair of spectra in which the intensity is the same can be
selected. The sector is divided to give readings of $\log I_0/I$.

The Hüfner instrument, although of classical design, has now been
superseded by instruments of the Nutting type. In this the photometer is
a separate unit from the constant deviation spectroscope and thus the latter
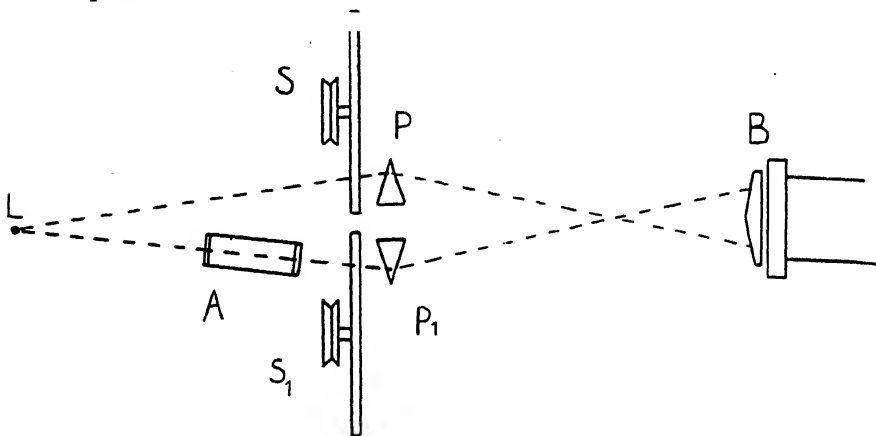

FIG. 23 (VII *)

can be used alone when necessary. The instrument is considered in more
detail in the next section. For very accurate work, particularly at high
densities, a modified form has been described by Dowell,[1] which follows
the tan.[4] θ law instead.

As regards the ultra-violet, the sector arrangement described is offered
by several manufacturers. The Spekker Photometer of Messrs. Hilger is
much speedier in operation and easier of adjustment. For approximate
measurements on substances liable to decompose on exposure to ultra-
violet light, or other causes, a single exposure of a few seconds with the
notched echelon cell suffices. The cell has been described by Twyman
and his collaborators.[2]

Grating Spectroscopes. These instruments differ from the ordinary
spectroscope in that they contain a diffraction grating instead of a prism.[3]

Grating spectroscopes may be used for the measurement of absorption
and emission spectra, the wave-length for any line of the grating spectrum
being proportional to the sine of the corresponding angle of deflection.
The head of the micrometer screw, by which the telescope is made to traverse
the spectrum, thanks to this property, is divided in terms of wave-lengths
so that the wave-length of any line may be read straight off.

In the Lowe and Schumm Evaluating Grating Spectroscope

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[1] *J. Sci. Inst.*, 1931, *8*, 382.   [2] See, e.g., *Proc. Phys. Soc.*, 1933, *45*, 1.
[3] For theory of diffraction, see Houston, *A Treatise on Light*, Chap. X, 1933 Edition.

(Fig. 24 (VII *)) made by Messrs. Zeiss, Jena,[1] the absorption bands are very clearly defined, so that the instrument is well adapted for the spectroscope's analysis of dyestuffs by Formánek's method, and for the study of blood spectra by Schumm's method. In order to render the cross lines clearly visible even within very dark absorption bands the telescope is fitted with a device which illuminates the cross-wires. A suitable source of light may be found in a bright filament lamp with a frosted bulb.
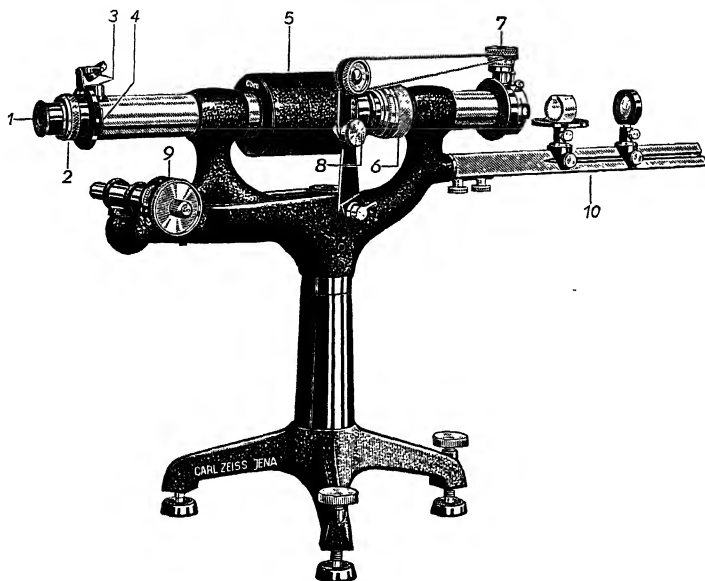
FIG. 24 (VII *)

Description of Grating Spectroscope. The spectroscope is set up on a heavy tripod with adjusting screws. The symmetrical precision slit can be adjusted, whilst observing the spectra through the telescope, by means of a cord transmission and the slit drum, 7. The slit is protected from external influences by a metal cap with a quartz window; the grating (142 lines to the millimetre) by the sleeve, 5. The graticule, which is focused by turning the milled ring, 2, can by means of the illuminating equipment, 3, be illuminated so that it is visible even in the dark regions of the spectrum (absorption bands). When it is desired to examine certain regions of the spectrum more thoroughly, these can be screened off by the diaphragm slide, 4. In this way they are prevented from being eclipsed by adjacent bright sections of the spectrum (bright spectral lines) and are more easily observed. The drum of the wave-length screw, 9, from which the wave-lengths are ascertained, is divided in Ångströms. A condenser lens and table for cells are carried on the optical bench, 10.

The absorption band spectrum of selenium has been examined by Nevin,[2] using a grating spectroscope, and is given here as an example of modern

[1] To whom acknowledgement is made for electro.
[2] *Phil. Mag.*, 1935, *20*, 347.

work in this field. The previous most complete investigation was that of Rosen,[1] who gave a vibrational analysis of the bands and showed that the wave-lengths agreed with those of heads in the emission spectrum and the fluorescence spectrum excited by white light. Two new systems lying in the regions $\lambda\lambda$ 2099–2895 and $\lambda\lambda$ 2758–3150 were discovered by Moraczewska,[2] in addition to a number of new bands belonging to the system analysed by Rosen. Olsson [3] has made a rotational analysis of five emission bands which also appear in absorption in Rosen's system and found they are due to a $^1\Sigma \longrightarrow ^1\Sigma$ transition. In addition, from measurements of bands due to the .molecule $Se_{80}Se_{80}$, he has shown that Rosen's values of v' must be increased by five units.

Nevin's [4] paper deals with the system described by Rosen. The dispersion Rosen used was very small (300 cm.$^{-1}$ per mm.) and the values of ΔG $(v + \frac{1}{2})$, which should be the same for any row or column of the table of v' and v'' progressions show large discrepancies, and many of the bands for low values of v'' are very diffuse.

The experimental procedure followed by Nevin was as follows :

The absorption cell was of fused quartz 15 cm. long and 3 cm. diameter, with flat ends of transparent fused quartz. After baking out, 0·01 gm. of pure selenium was introduced and the cell re-exhausted with an oil diffusion pump, backed by a Hyvac pump, and sealed off. It was inserted in an iron tube, which could be heated electrically to about 900°. As sources of continuous spectrum a water-cooled hydrogen tube of the Bay and Steiner [5] pattern, taking 1 amp. at 3,000 volts, was used up to λ 3650, and a tungsten filament lamp above this point. Photographs of the absorption spectrum were taken at different temperatures in the second order of a two-metre grating in a stigmatic mounting, with a dispersion of 8·8 Å./mm., and in the first order of a 21-foot grating in an Eagle mounting, with a dispersion of 2·6 Å./mm. An iron comparison spectrum was used. On the large grating plates the heads above λ 3500 were obscured by the overlapping rotational structure of other bands. The wave-lengths of the stronger heads below this point are probably correct to about 0·03 Å. The heads above λ 3500 have been measured only on the small grating plates.

A vibrational analysis was made and large perturbations of the heads belonging to a number of levels were found. An isotope effect has also been observed and good agreement is found between the observed and calculated positions of the heads.

Applications of Absorption Spectrophotometry. The practical applications of absorption spectrophotometry have been summarized by Morton.[6] He includes (1) inorganic and organic substances, (2) analytical applications, (3) biological problems, and infra-red spectrophotometry.

[1] *Zeits. f. Phys.*, 1927, *43*, 69.   [2] *Ibid.*, 1930, *62*, 270.
[3] *Ibid.*, 1934, *90*, 140.   [4] *Loc. cit.*   [5] *Ibid.*, 1927, *16*, 337.
[6] *Inst. of Chem.*, London, 1938.

SECTION 2: SPECTRUM ANALYSIS

Quantitative Analysis using the Visible Spectrum. In Gerlach's internal standard method one or more lines of an impurity are compared with one or more neighbouring lines of the substance containing it.

With the Twyman apparatus (Hilgers) a small handle at the eyepiece can be turned so as to displace the lower part of the spectrum relatively to the upper: in this way it is generally possible to get one of the lines due to the impurity in line with one of those of the same colour due to the main constituent. A neutral tint wedge of graduated density with a scale attached is then moved so as to reduce the intensity of the main spectrum line till it matches that of the line due to the impurity, the amount of reduction necessary being read off on the scale. From a number of standard specimens of known analysis a curve can be drawn for any particular line giving the wedge reading for different percentages of the impurity. The method may be expected to be accurate within 5 per cent of the amount of impurity present in favourable circumstances. For metals or powders the arc is used, while for solutions the spark method using the Hitchen's tube may be employed.

Hitchen's Tube for Quantitative Spark Spectra. A glass reservoir fitted with a tap and holding about 25 ml. is connected by a long capillary to a U which opens out into a wider bore, the upper end of which supports a short silica jet surrounding a gold wire electrode. The upper electrode may be a stout gold wire or a pure graphite rod tapered to a point. The spark gap is surrounded by a wide glass tube to stop spray and to collect the liquid: it has a small circular window transparent to the ultra-violet. When sparks are passed the solution is atomized and is replaced by fresh solution from the reservoir.

When alternating current is available the spark is best obtained with a $\frac{1}{4}$ kilowatt tapped transformer and a 0·005 microfarad condenser: with a tapped self-induction coil (0·03–1·0 millihenries) in series with the spark the air lines can be cut out of the spectrum.

In the Nutting Absorption Spectrophotometer (see previous section) two beams are obtained from the same light source, preferably a Pointolite lamp, by means of an optical device. The one beam is cut down in intensity by the absorbing medium placed in it, while the other is reduced in the same proportion by means of two polarizing prisms, one of which can be rotated. The beams are brought into close juxtaposition by another optical device whose edge is sharply focused upon the spectroscope slit. As described, this instrument also obeys the law $I/I_0 = \cos^2 \theta$. Some advantage accrues from placing another polarizing prism in the beam containing the absorbing medium, this prism being set to polarize in a plane at right angles to that of the prism in the other beam. The instrument then obeys the law

$I/I_0 = \tan^2 \theta$, and the scale is more open at the high density end. The spectrophotometer is shown diagrammatically in Fig. 25 (VII *). Light from the Pointolite lamp, H, passes through two windows in a metal screen and the two achromatic deviating prisms E, emerging as two axially parallel beams. These beams pass through the absorption tubes D_1 and D_2 respectively and into the windows A and B of the photometer where they fall on the prisms J_1 and J_2: these are square-ended polarizing prisms with their polarizing planes perpendicular to one another, so that after passing through them each beam is polarized, but in a plane at right angles to that of the other. The prism K brings the two beams close to one another.
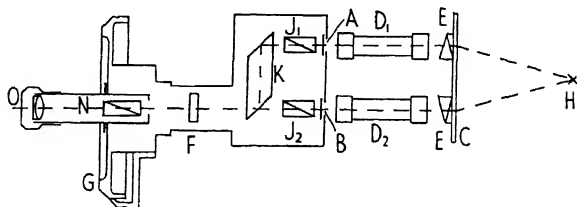

FIG. 25 (VII *)

The light next passes through the third polarizing prism N which is mounted on a circle so that it can be rotated; finally the object glass O focuses an image of the dividing-line on the slit of the spectroscope. By rotating N the intensity of one-half of the field is diminished while that of the other half is increased. With the same liquid in both tubes the polarizing plane of N will obviously be at 45° to that of either J_1 or J_2, and this will be the zero reading.

With different solutions in D_1 and D_2

$$I_0/I = \tan^2 \theta$$

where I_0 = intensity of light incident on A
  I = intensity of light incident on B
  θ = the angle through which N is rotated to get equality of intensity in the two halves of the field.

Wave-length Spectrometers for use in the Ultra-violet. In the latest model of their constant deviation wave-length spectrometer, Messrs. Hilger have made arrangements so that the instrument can readily be converted for use in the ultra-violet or the infra-red.

The tripod of the instrument can be attached to a rigid bar, 42 inches long, which acts as an optical bench and is positively in alignment with the collimator axis. The stands for all accessory apparatus are made to fit this bar.

For the ultra-violet the telescope drawtube is removed and a quarter-camera put in its place : this camera, together with the object glass of the telescope, forms an optical system on the telephoto principle having an equivalent focal length of 53 mm. The carriage of the plateholder can be moved vertically by a rack and pinion so that it is possible to take 24 spectra on one plate. With the prism $\mu_D = 1.65$ the spectrum up to $\lambda = 3,650$ Å can be photographed; the spectrum from 4,060–6,100 Å being 31 mm.

long : with the prism $\mu_D = 1\cdot74$ the limit is 3,850 Å, but the length is 60 mm.

For a more extended range in the ultra-violet a quartz spectrograph must be used.

The instrument can be converted into an *ultra-violet monochromator* by removing the prism, telescope, and collimator and replacing the last two by mirrors and the first by a Cornu prism. This is a quartz prism consisting of two 30° prisms of right and left rotation put in optical contact to form a 60° prism. The collimator mirror has a focal length of 27 cm. Symmetrical slits are provided for the collimator, while those for the telescope have a block with a recess for a thermopile (when required) and an eyepiece for observation of the thermopile and the slit. The wave-length drum is also changed.

The image of the light source on the slit is produced by a mirror. This instrument may be used instead of a quartz spectrograph, although this is not recommended by the makers. Accessories for use as a spectrometer include a fluorescent eyepiece, a thermopile or photoelectric cell with quartz window and a camera to go in place of the telescope mirror.

Ultra-violet Spectrophotometer. The determination of the absorption spectrum in the ultra-violet has of recent years greatly increased in practical importance and is now used, for example, in routine determinations of vitamins A and C and the synthetic vitamin D.

The method consists in determining the *extinction coefficients* at various wave-lengths. When light of intensity I_0 passes through a layer of the medium of thickness 1, the emergent light has an intensity I, where

$$I_0/I = 10^{k1}$$

and k is called the extinction coefficient. Log I_0/I is called the density.

Light from a single source is divided into two beams, one of which has its intensity lowered by passing through a layer of the absorbing medium, while that of the other can be reduced by known amounts : this device forms the photometer. The two beams then pass through a quartz spectrograph which resolves them into spectra, and photographs are taken of a series of spectra in which the intensity of the variable beam is successively reduced. The spectra are then examined at each wave-length to see in which the absorbed and reduced lines are of equal intensity, and from these results a curve is plotted showing extinction coefficients against wavelengths.

Various methods may be used for reducing the intensity of the comparison beam : the duration of intermittent exposures may be varied ; this method is not very rapid : polarization may be used, but here there is an initial loss of 50 per cent of the available light : in the Spekker instrument made by Hilgers each path has an aperture, one being fixed and the other variable by means of a shutter mechanism operated by a screw. The two light paths are then brought into juxtaposition on the slit of the spectrograph by means of a rhomb. All the optical parts and also the cells to contain the liquid are made of quartz.

The quartz spectrograph has a quartz Cornu prism and quartz lenses for the telescope and collimator : with the Barfit medium model the spectrum

is from 2,000 Å to 10,000 Å and is 225 mm. long.   Plateholders to fit the
camera and to take various sized plates may be obtained.

Light Sources. A high-tension spark between tungsten-steel elec-
trodes is most satisfactory for medium dispersion.   Uranium electrodes give
a more continuous spectrum such as is desirable with higher dispersion :
they disintegrate rapidly and are expensive.

When photoelectric methods are used for the comparison of the spectrum
pairs a continuous spectrum such as that obtained from a hydrogen dis-
charge tube with a rocking mirror device to correct the non-uniform dis-
tribution of the intensity is employed.

Various types of quartz cell are obtainable, using liquid thicknesses
from 0·1 mm. to 20 mm.

Photoelectric Absorption Apparatus for the Ultra-violet. The
principle of the use of the photoelectric cells is somewhat similar to that
used in the Spekker absorptiometer (q.v.). (See also Chap. VI *, 5, 8.)

A small part of a beam of light from a monochromator is reflected into
one photoelectric cell by a quartz plate.   The rest of the beam passes
through a quartz cell containing the substance whose absorption is to be
measured, through a revolving sector which is fully open and then into a
second photocell.   The two cells in opposition are connected to a Linde-
mann electrometer and the potentials on the cells are so adjusted that the
electrometer shows no deflection (the cells are the alkali metal type).   A
comparison cell is then substituted for the cell containing the solution and
the electrometer deflection is again restored to zero, this time by reducing
the opening in the revolving sector.   The ratio of the transmission of the
sector when so adjusted to its transmission when fully open is the same as
that between the absorption tube and the comparison tube and so is a
measure of the absorption of the substance for the particular wave-length
used.

The revolving shutter is adjustable while it is running.   It consists of
a metal cylinder mounted with its axis perpendicular to the beam of light.
The end of the cylinder is cut in the shape of a rectangular spiral so that
when it is moved along its axis, the fraction of a complete revolution during
which the light is cut off can be varied continuously from 0 to 1 and the
variation is proportional to the movement.   The amount of movement is
indicated on a scale whose calibration is not subject to loss of accuracy
through wear.

SECTION 3 : INFRA-RED SPECTROSCOPY

For the infra-red the ordinary spectrometer with lens and prisms a.
described in the previous chapter may be used up to $\lambda = 20,000$ Å $(2\mu$
by using the slit with the thermopile mount in place of the eyepiece of th(
telescope. The thermopile is of the linear type with the sensitive are:
20 mm. by 1·5 mm., the junctions being bismuth-tin to bismuth-antimony
The light source is a Pointolite lamp.

Extension to 21μ. For this purpose the lens system is replaced b)
the mirror system described above for the ultra-violet, and again the eye
piece with the thermopile is used.

Prisms suitable for different parts of the spectra are as follows :

Quartz	visible to		$3\cdot5\mu$
Fluorite	visible from	3μ to	9μ
Rocksalt	„	„ 8μ „	17μ
Sylvine	„	„ 15μ „	21μ
Potassium bromide	„	„ 19μ „	28μ

The quartz has the greatest dispersive power and the order is then fluorite
rocksalt, and sylvine. The rocksalt prism, owing to its hygroscopic nature
is varnished with a solution of pyroxylin in amyl acetate. In the case o
quartz and fluorspar the natural crystals are employed. In the othe:
crystals employed the artificially produced crystals are suitable. For th(
production of large crystals of potassium bromide, see Chapter IV*
The Nernst glower is a convenient source of continuous infra-red radiation
It is made up of a filament 3 cm. long by 1 mm. in diameter and is compose(
of oxides of rare earths. It is heated from a battery or other constan:
voltage source, taking 1 amp. at 110 volts.

The technique in infra-red work is difficult. Stair and Coblentz[1] hav(
examined the infra-red adsorption spectra of plant and animal tissue usin{
a mirror spectrometer, portable vacuum thermopile, and ironclad Thomso1
galvanometer as far as region 15μ. The work of Robertson Fox anc
Hiscocks[2] is the first of an important group of papers describing the us(
in accurate work of dispersing prisms. In a paper by Snow and Taylor
the use of gratings is well discussed. In a recent paper by Fox anc
Martin[4] on the study of some hydroxy compounds in the region of 3μ
an echelette grating in conjunction with a rocksalt prism was employed

Their echelette grating was ruled by Professor R. W. Wood, with 2,05(
lines to the inch, on a concave surface of 1 metre focal length. This wa:
used in conjunction with the rocksalt prism spectrometer, thermopile anc
galvanometer system which have previously been described by Robertson

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[1] *J. Res. of the Nat. Bur. St.*, 1935, *15*, 295.
[2] *Proc. Roy. Soc.*, 1928, *120*, *A*, 128.   [3] *Ibid.*, 1929, *124*, 442.
[4] *Ibid.*, 1937, *A*, 419–41, 421.

Fox, and Martin.[1] The second-order spectrum was selected for the 3μ region and calibration effected by visual observation of appropriate orders of the Hg line λ 5,460·7. All wave-lengths given in this work for sharp bands may be regarded as accurate to $\pm$ 0·001μ. Slits were adjusted so that a galvanometer throw of 10–20 cm. was obtained, and under these conditions it was possible to obtain the fine structure of lines less than 2 cm.$^{-1}$ apart.

Absorption cells were constructed with fluorite plates cemented to a brass ring by means of a film of fish glue, and three sizes of cell were used varying from 1·3 to 10 mm. in length. Two similar absorption cells were selected, one containing solution and the other solvent, and these were placed alternately in the light path for measurements at each wave-length, so that reflexion and other losses would be compensated.

When the absorption is nearly complete the calculated value of the extinction coefficient is greatly influenced by the presence of a small amount
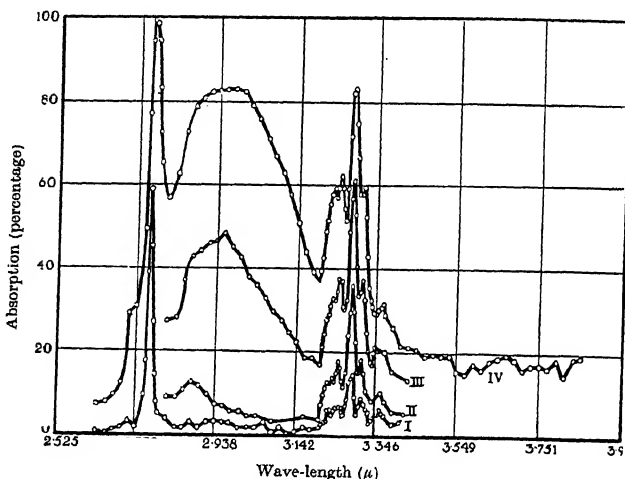

Wave-length (μ)

FIG. 26 (VII *)

of stray light in the spectrometer. This effect was found to be most pronounced on very sharp absorption bands, and it was allowed for in their calculations by observing the light apparently transmitted through a highly concentrated solution which is known to absorb completely at the desired wave-length.

A typical infra-red spectra curve for a 1·29 mm. layer of phenol in carbon tetrachloride at different concentrations is shown in Fig. 26 (VII *). I represents 0·0145, II 0·0435, III 0·087 and IV 0·174 mol./l.

There is considerable difference in the absorption spectra of isotopic molecules,[2] but the absorption may lie in an inconvenient region of the spectrum (with methane in the Schumann ultra-violet) with the large change in vibration frequency obtained by the introduction of deuterium atoms into the molecule and also to the splitting of degenerate energy

[1] *Phil. Trans.*, 1934, A, *232*, 463.
[2] Cf. Melville, *Sci. Prog.*, 1938, *32*, 522.

levels of the molecule, the infra-red absorption spectra give striking difference when O atoms replace H atoms in the hydride. The technique for the study of the infra-red spectra of such compounds, e.g. methanes and ethanes, has been extensively investigated by Benedict, and others.[1]

A summary of the apparatus and types of grating used for various parts of the spectrum is excellently reviewed by Sutherland.[2] In 1928 it was shown by Raman that a new type of secondary radiation exists. This branch of physical chemistry has developed enormously and it is considered separately in the next section.

[1] *J. Chem. phys.*, 1937, *5*, 1.
[2] *Infra-red and Raman Spectra* (Methuen), 1935.

SECTION 4 : THE RAMAN EFFECT

Introduction. A new and simple method of investigating molecular structure has been developed within the past few years, based upon the discovery made by Raman in 1928, that a beam of monochromatic light has its frequency altered when scattered by a liquid, in a way which depends intimately on the nature of the scattering molecules. Subsequently it has been shown that this abnormal scattering, now called the Raman Effect, is exhibited not only by liquids, but by practically all gases and crystalline solids ; that the scattering lines depend only on the type of scattering molecule ; and, most important of all, that the difference in frequency of the incident light and that of the lines in the scattered light are equal to the characteristic frequencies of the molecule.

Apparatus and Experimental Method. Raman illuminated the fluids freed from dust in spherical glass bulbs, concentrating the light of a mercury arc at the centre of the bulb by a large lens, and photographing the scattered light end-on. In this method long exposures were necessary to obtain the scattered lines. A great improvement in the technique was introduced by Wood. His apparatus consists of a glass tube of 3 cm. internal diameter (Fig. 27 (VII *)), blown flat and thick at one end, and
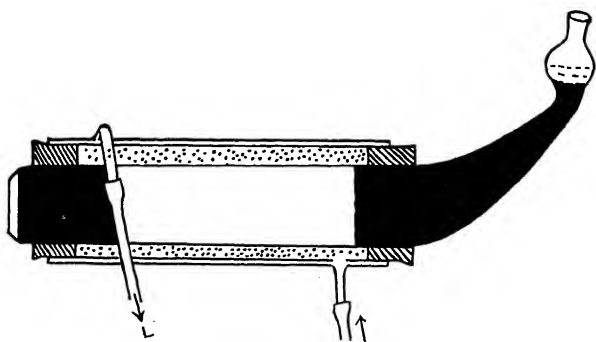
FIG. 27 (VII *)

drawn off into an oblique cone at the other. The flat end is ground plane and polished, or is made sufficiently good optically by cementing a thin cover-glass to the ground surface with Canada balsam. The inner tube is surrounded by a jacket, through which water is circulated in order to prevent rise in temperature.

A small bead of glass is fused into the wall of the sloping cone, so as to coincide as nearly as possible with the axes of the tube. This bead, backed by a lamp, appears as a bright spot when viewed through the other end of the tube, and presents a method of adjusting the tube parallel to the axis

of the collimator. Portions of the tube are painted black as indicated in the diagram.

The mercury arc is placed a few inches above the tube as shown in Fig. 28 (VII *). It should be mounted in some type of non-metallic support to minimize heat transference to the tube by conduction. Two reflectors are employed to augment the illumination. These are shown in Fig. 28 (VII *), one being placed above the arc, the other fitting around the underside of the inner tube.

In this way practically the entire emission of the arc is thrown into the tube, and Raman lines can be obtained by comparatively short exposures.

The aiming of the spectroscope is a matter of importance if scattered light from the walls of the tube is to be arrested. Wood accomplished this by mounting two diaphragms, perforated with square holes 1 cm. in diameter, about 30 cm. apart. An incandescent lamp was placed near the glass bead, and the screen adjusted, so that the bead was visible when viewed through the two holes. The spectroscope was now placed with its slit some 20 cm. from the first screen, and the collimator pointed through the two holes at the illuminated head. The focusing-point of the spectrum was next observed, and with the slit wide open, the instrument was adjusted so that the illuminated bead was seen exactly at the centre of the camera lens. The lamp

FIG. 28 (VII *)

was now removed, and a lens of about 18-cm. focus was placed close to the first screen, giving an image of the hole in the second screen in the slit of the spectroscope. The slit was then closed and the exposure made.
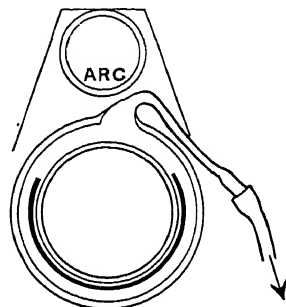
Wood employed a Bausch and Lomb one-prism spectrograph, with a comparison spectrum of the iron arc running across the centre.

The mercury arc, if used directly, has at least five lines which are strong enough to give rise to Raman lines, and a plate secured from such a source will have so many lines that the pattern from each exciting line will overlap, and identification will be difficult. The number of exciting lines may be cut down by employing suitable filters. This is accomplished in Wood's method by dissolving the coloured material used as a filter in the water operating the cooling system. Difficulty is met in the case of certain substances which decompose under the action of light. This difficulty has been partly overcome by keeping a stream of the substance flowing through the Raman tube.

Theory of Raman Spectra. The Raman effect is analogous to a scattering effect produced in X-rays by ' face ' electrons, which was discovered some years earlier by Compton. Both constitute excellent experimental evidence of the quantum theory of light, and the application of the theory to the Raman Effect may be summarized as follows :

A monochromatic beam of light of frequency ν_1 has its energy distributed in small bundles or ' quanta '. Each quantum consists of the same amount of energy E_1, an amount which may be determined by multiplying

the frequency of the light ν_1 by the universal constant h, known as Planck's constant. Thus,

$$h\nu_1 = E_1 \qquad . \qquad . \qquad . \qquad . \qquad . \quad (1)$$

The same property of possessing energy in quanta appears in molecules and atoms. The atoms constituting a molecule possess energy of vibration due to thermal energy; the frequencies of these vibrations constitute the infra-red frequencies characteristic of the molecule. Thus a molecule, consisting of two atoms with some force holding the nuclei normally a fixed distance apart, will have one characteristic vibration frequency ν_m, due to the vibration of the atoms toward and away from each other. If quantum principles apply to the absorption of energy by such a molecule, it can only absorb energy in multiples of a single quantum E_m, characteristic of its frequency ν_m, i.e.

$$E_m = nh\nu_m \quad . \qquad . \qquad . \qquad . \qquad . \qquad . \quad (2)$$

where $\qquad\qquad n = 1, 2, 3,$ &c.

If a light quantum parts with some of its energy to such a molecule, it can only do so by losing amounts of energy given by (2), being itself scattered as a quantum of diminished frequency ν_2.

In the simplest case $n = 1$. Such a scattering process gives:

$$E_2 = E_1 - E_m$$

or $\qquad\qquad h\nu_2 = h\nu_1 - h\nu_m$

whence $\qquad\qquad \nu_1 - \nu_2 = \nu_m \qquad . \qquad . \qquad . \qquad . \qquad . \quad (3)$

Thus the frequency of the scattered light is always less than that of the incident light, and the difference in frequency $(\nu_1 - \nu_2)$ between the incident and scattered lines in the Raman Effect correspond to that of the infra-red frequency ν_m characteristic of the molecule.

Raman Lines and Molecular Structure. The most striking confirmation of the above theory appears when Raman lines due to a number of different compounds are classified according to their chemical structure. It is then found that the Raman pattern is determined entirely by those factors which most affect the nature of vibration, namely:

(1) The number of atoms in the molecule.

(2) The masses of the atoms.

(3) The strength of the chemical bonds between the atoms.

These facts can be simply illustrated, if the lines due to some diatomic molecules are considered. Assuming that the mode of vibration of the atoms in these molecules consists of their to and fro movement along the line joining their nuclei, the system may be likened to the mechanical oscillation of two spheres attached at their centres by a spiral spring. An application of elementary mechanics shows that the frequency of vibration of such a system is given by

$$\nu = \frac{1}{2\pi} \frac{F}{\mu}$$

where F represents the force arising when the balls are displaced unit distance from their equilibrium position, and μ is a function of the masses of the balls.

If the vibration of the atoms in a diatomic molecule conform to this mechanical analogy, then it is obvious :

(1) That a molecule containing light atoms should have a higher infra-red frequency than one containing heavier atoms.

(2) That a molecule in which the force binding the atoms is great should have a higher characteristic frequency than one in which the force is weak. These forces depend on the strength of the interatomic bonds, so that a diatomic molecule with a double bond might be expected to have a higher characteristic frequency than one containing only a single bond.
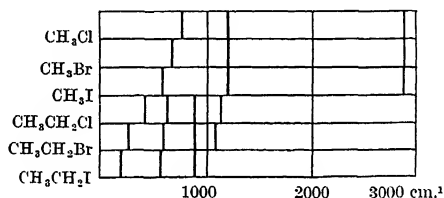
FIG. 29 (VII *)

The correctness of this argument is excellently borne out in the series of Raman lines exhibited in Figs. 29 (VII *) and 30 (VII *).

The diagram is simplified by arranging all the existing lines on the zero axis, the values given at the bottom indicating the change in frequency of the Raman lines $(\nu_1 - \nu_2)$.

An examination of the figure shows that the lightest atoms have lines of high frequency, as the substitution of a halogen atom for one of the hydrogen atoms in the H_2 molecule giving HCl, HBr and HI, lowers the frequency,
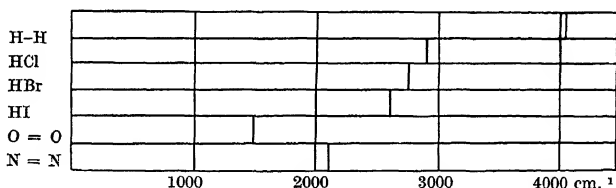
FIG. 30 (VII *)

the decrease being greatest in the case of HI, Iodine being the heaviest atom. It is evident, furthermore, that strengthening of the bond between the atoms in a diatomic molecule further lowers its characteristic frequency, as is shown by the shifting of the Raman lines for nitrogen and oxygen. Actual Raman spectra indicate that the rates of strength of single : double : treble bonds is $1 : 2 : 3$.

A second class of compound, not quite so simple as the diatomic type, gives a Raman spectrum consisting of *one line* accompanied by other groups of faint lines of much higher frequency. This class is comprised of molecules [1] which have two heavy atoms, but contain, in addition, some hydrogen attached to one or other of the heavier atoms. Examples of this class

[1] Cringler, *Phys. Rev.*, 1931, 38.

would be the methyl halides—they are classified as quasi-diatomic molecules. The hydrogen is so light that its motion does not appreciably affect the relative motion of the two heavy atoms, so that the Raman lines consist of single lines obeying the same rules as those exhibited by diatomic molecules, and in addition some lines of higher frequency due to the hydrogen (Fig. 29 (VII *)).

Triatomic molecules will have a more complex series of Raman lines, since there will in general be three frequencies characteristic of such molecules. The presence of hydrogen in such molecules will produce extra higher frequency lines in the same way as in the case of quasi-diatomic molecules. Thus a molecule like $CH_3 - CH_2Br$ gives three Raman lines, due to the frequencies of relative vibrations of the three heavy atoms, and three extra weak lines due to the vibration of the hydrogen atoms.

As in the previous case the manner in which the main lines shift, as the weight of one of the heavier atoms changes, is what should be expected from the theory of such vibrations (Figs. 29 (VII *) and 30 (VII *)).

Development of the theory outlined above for the simpler types of molecule has led to a complete scheme of identification for the Raman patterns of a great many substances, and consequent elucidation of their molecules and spectra. Complex Raman patterns are formed by simultaneous vibration of the atoms in the molecule, and it is possible to designate the different portions of the spectrum associated with various groups, of which the mode of vibration has been determined by a study of similar spectra.   .

Some Applications of Raman Spectra. (a) *Isomerism.* The application of Raman Spectra to the study of isomerism has already met with some success, notably in connection with keto-enol and cis-trans-isomerism. For further details the reader should consult original papers.

(b) *Dissociation of Electrolytes.* It would seem that a large field of research should be opened up by the application of the Raman Effect to the study of the Dissociation of Electrolytes. It is obvious that a dissociated molecule (diatomic) would contribute nothing to a normal Raman Spectrum, since the dissociated atom would not be in a state of vibration. A partly dissociated liquid should contain, therefore, molecules some of which contribute towards the intensity of the Raman Spectrum and some which contribute nothing, so that a measurement of Raman line intensity might be expected to indicate in some way the degree of dissociation of the electrolyte. The new refined and accurate method of microphotography developed by Moll provides an accurate means of estimating the intensity of Raman lines—an alternative method of recording spectral line intensity has been described.

(c) Attempts have been made successfully to apply the Raman Spectra to measure approximately the amount of the constituents in a mixture by measuring the change in intensity with composition of the lines in the spectra. An analytical method of the type might be applied in following the course of certain chemical reactions, the intensity of the Raman lines due to one of the reacting molecules being measured by a Moll microphotometer.

(d) The Raman Spectra of a great number of inorganic and organic

substances under various conditions have been determined and numerous relationships deduced, e.g. the Raman spectra of benzene and derivatives has been studied by Kohlraush,[1] of tetra alkyls by Anderson,[2] of phosphoric acids by Venkateswaran,[3] of sulphuric and nitric acids by Chédin,[4] and of rubber by Gehman and Osterhof.[5] All phases of the Raman effect, including a summary of several hundred investigations on this problem, are dealt with in a monograph written by Hibben.[6]

[1] *Phys. Zeit.*, 1936, *37*, 58.   [2] *J. Chem. Phys.*, 1936, *4*, 161.
[3] *Ind. Acad. Sci. Proc.*, 1936, 3A, 25.   [4] *Comp. rend.*, 1936, *202*, 220.
[5] *J. Amer. Chem. Soc.*, 1936, *55*, 215.
[6] *The Raman Effect and its Chemical Applications*, Reinhold Pub. Co., N.Y., 1939.

SECTION 5: X-RAY CRYSTAL ANALYSIS

Within the last decade the study of the crystalline structure of matter has developed with great rapidity. In the year 1912, at the suggestion of Von Laue, it was demonstrated that X-rays could be diffracted by a crystalline substance. As a result of this experiment he was able to show that X-rays were the same form of wave motion as ordinary light, but of considerably shorter wave-length. It was Bragg, however, who pictured the process of X-ray diffraction and showed that by utilizing the regular atomic planes within a crystal, X-rays were diffracted according to the law,

$$n\lambda = 2\alpha \sin \theta$$

where λ = wave-length of the X-radiation (in Ångstrom units)

α = Spacing in Å. units, of the geometrically like crystal planes.

θ = Glancing angle between the incident X-ray beam and the reflecting plane.

n = A small whole number, which represents the order of reflection.

This condition is fulfilled when X-rays are reflected from those internal layers of geometrically like planes of a crystal, which present an angle with the incident X-ray beam such that the reflection from each layer reinforces that from each other layer. A strong diffracted X-ray beam is the result. At other angles of incidence, the reflection from each layer interferes with that from each other layer, the resultant beam being of very feeble intensity. It should be remembered that use of the word 'reflection' is made to help to picture the process of X-ray diffraction. X-rays are diffracted by a crystal, but may be spoken of as being reflected from a particular crystallographic plane.

The equipment for the study of the crystalline structure of matter then, consists of two parts:

(a) a device for exciting monochromatic X-rays of known wave-length (λ).

(b) a device for suitably recording diffracted X-rays, and permitting of measurement of the angle of diffraction (θ).

X-ray Excitation. X-rays are a wave motion of very short wave-length and are radiated when an electron from either of the M or L orbits of an atom moves to an orbit nearer to the nucleus. An X-ray tube is therefore a means of supplying energy to cause electron movements in the atoms of the material forming the target.

The tube is made up of an efficiently insulated cathode contained in an evacuated space. The cathode is made to emit electrons and with the application of a suitable potential the electrons acquire a high velocity and pass across the evacuated space to bombard the target of the X-ray tube. Here the sudden arrest of the electrons and therefore the sudden

absorption of energy by the material of the target causes the radiation of X-rays. The cathode may be made to liberate electrons by two means :

(i) By the means employed in a gas type of X-ray tube, where the residual amount of gas retained in the tube is ionized by the high tension of the cathode, the positive ions bombarding the cathode to liberate electrons.

(ii) By the means employed in a hot cathode X-ray tube, where a tungsten filament is heated to the temperature at which it gives off an abundant number of electrons.

In both types of tube the electrons are focused to the target and are prevented, by shielding from bombarding the walls of other parts of the tube.

In accordance with the Bragg formula, $n\lambda = 2d \sin \theta$, the X-radiation to be diffracted by a crystal must be monochromatic and of known wavelength. The X-ray spectrum emitted by the target is composed of two distinct sets of lines super-imposed upon a continuous range of wave-lengths termed 'white radiation'. The strongest line of the harder of the set of lines is chosen for crystal analysis work, and is termed the $K\alpha$ doublet, it is also the longest wave-length of this series. It is impossible, however, to excite the $K\alpha$ doublet without exciting the remaining lines of the series, and the line is therefore isolated by the use of a filter. A filter for a particular radiation is chosen because of the element having a sudden increase in absorptive power for X-rays, at a wave-length corresponding to that of the $K\beta$ line of the particular radiation chosen. For example, Ni has a sudden increase of absorption for X-rays at a wave-length corresponding to the $K\beta$ line of the Cu X-ray spectrum. Ni therefore absorbs the $K\beta$ line and is then a suitable filter for Cu radiation. A thickness of 0·002 mm. of Ni is sufficient to monochromatize Cu radiation generated by an optimum potential of 50 kilovolts (peak). Similarly a filter of 0·0017 mm. of Mn will monochromatize Fe radiation generated by an optimum potential of 40 kilovolts peak.

In order to facilitate the accuracy of measurement of the diffraction angle θ, radiation of as long a wave-length as expedient, to give a maximum dispersion, should be used. The choice of radiation is, however, controlled by a number of factors :

(i) Radiation generated from elements lower in the Periodic table than Cr is so readily absorbed in air, that its use is impracticable other than with a vacuum camera.

(ii) The scattering factor of the specimen to be analysed for the radiation chosen, to be a minimum.

(iii) Material forming the target to be capable of electronic bombardment for long periods, under suitable conditions, without melting.

For these reasons then radiation from targets of metals between atomic numbers 24 Cr to 29 Cu will be found to be most useful. Radiation from Ag, Mo and W targets may also be of value. Thus for the successful analysis of a wide range of crystals, it is essential that the design of X-ray tube permits the ready change of target.

In order that exposures in crystal analysis work be as short as possible, amongst other things, the X-ray tube should emit a maximum intensity of radiation. One of the factors controlling intensity of the radiation is the material of the window. In most tubes of the demountable type the

window is made of Al foil. A marked improvement is now being made by the use of thin sections of Be metal, and the resultant increase of intensity is by a considerable factor. A window of this metal is of extreme value in the analysis of organic compounds, where, even under the best of conditions, exposures are very long.

Demountable tubes of both the hot cathode and gas type which fulfil the above conditions are manufactured by Messrs. Adam Hilger, Ltd., and full particulars of them may be obtained from that firm.

X-ray Crystal Analysis.[1] In order that the explanations which follow may be better understood a short account is here given of the structure of crystals. A crystal owes its symmetry to the perfectly regular arrangement of its atoms in a space pattern. Suppose the atoms comprising this pattern be grouped into small units such that the crystal can be built up by simply placing these units together, and a point be taken in each of these units (for example, the centre of a particular atom), we obtain a series of points in space such that each one is situated similarly to every other point. A number of points conforming to such an arrangement is obtained when space is divided into a number of parallelepipeds by three sets of parallel planes, the spacing of each set being constant, but not necessarily the same for all sets, and the different sets making any angle with one another. The points of intersection of these planes give the system of regularly situated points which constitutes the space lattice of a crystal.

FIG. 31 (VII *)
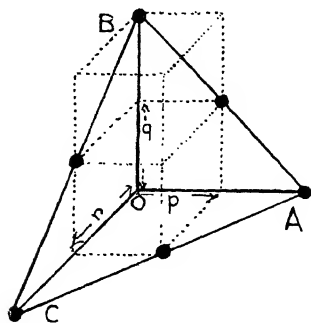
Theoretical consideration of the above would indicate that the number of possible space lattices on which crystals might be built is infinite, but the older crystallographers found from measurements with the goniometer, and X-ray measurements have confirmed, that the number of space lattices on which crystals are actually built is strictly limited. For an account of crystal systems, see Chapter II, S. 3.

Directions parallel to the three edges of an elementary parallelepiped are called the axes of the crystal. If these are all equal and mutually at right angles the elementary parallelepiped is a cube, and a crystal built on such a space lattice belongs to the cubic system. Let the lengths of the three sides of an elementary parallelepiped (Fig. 31 (VII *)) be p, q, and r, and let a crystal plane intercept these axes in A, B, and C respectively ; then

$$\frac{p}{OA} : \frac{q}{OB} : \frac{r}{OC} :: h : k : l$$ where h, k, and l are found by measurement to be small whole numbers seldom greater than 6 for any of the naturally developed crystal faces. In the figure, if the crystal is built on a cubic space lattice,

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[1] The authors are indebted to Messrs. A. Hilger, Ltd., London, who have supplied a large amount of information as well as diagrams for this chapter. Special thanks is also due to F. Twyman, F. Simeon and F. Brech of this firm for many helpful suggestions.

$\frac{p}{OA} = \frac{q}{OB} = \frac{r}{OC}$, and the plane ABC is called the (1.1.1.) plane of the crystal. The developed faces of a crystal of rock salt are the (1.0.0.), (0.1.0) (0.0.1), &c., according as they are parallel to the plane containing the q and r axes, the p and r axes, and the p and q axes respectively. They all belong to the same type, however, namely, the faces of a cube, and are usually spoken of as the {100} faces, the bracket indicating that the indices denote a type and not a particular face.

The cubic system is considered in a little more detail, firstly, as showing the reasoning on which certain structures are assigned to crystals ; and, secondly, because in the X-ray spectrography of the elements crystals of the cubic system are mainly used to 'reflect' the rays. When all the possible arrangements of points on a cubic space lattice are considered we find that there are in all three arrangements which may be referred to the cubic system.

(a) Points at the eight corners or 'Simple Cube Lattice '.

(b) Points at eight corners and face centres or 'Face-centred Cube Lattice ' ; and

(c) Points at eight corners and cube centres or 'Cube-centred Lattice '.

The ratios of the reciprocals of the spacings of the {100}, {110}, and {111} planes are important in X-ray analysis of cubic crystals and are here given as calculated from a simple geometrical figure.

$$\text{For } (a) \quad \frac{1}{d_{\{100\}}} \cdot \frac{1}{d_{\{110\}}} \cdot \frac{1}{d_{\{111\}}} \quad 1 : \sqrt{2} : \sqrt{3}.$$

$$\text{For } (b) \quad \frac{1}{d_{\{100\}}} : \frac{1}{d_{\{110\}}} : \frac{1}{d_{\{111\}}} :: 1 \quad \sqrt{2} : \frac{\sqrt{3}}{2}$$

$$\text{And for } (c) \quad \frac{1}{d_{\{100\}}} \cdot \frac{1}{d_{\{110\}}} \cdot \frac{1}{d_{\{111\}}} \quad 1 : \frac{1}{\sqrt{2}} : \sqrt{3}.$$

Although it has been convenient so far to speak of only the measurement of the diffraction angle θ, and therefore of the consequent knowledge of the spacings between sets of geometrically like planes, the crystal analysis of a substance also requires the determinations of its symmetry, space groups, crystal form, lattice parameter, and of its atomic formation. Many methods of analysis have been devised, each specializing in most readily yielding information of a particular kind.

Laue Method. The classical experiment suggested by Von Laue, of examining the diffraction of X-rays by a crystal, differs entirely from all succeeding methods of analysis. The method uses the 'white radiation ' emitted by an X-ray tube, and therefore radiations from either an Ag, Mo or W target is advisable, since below a potential of 50 kilovolts R.M.S. the characteristic radiation remains unexcited. A slit system which defines the X-ray beam, is set up in front of the window of a tube and the collimated rays made to fall on a crystal supported just beyond the slit system. A photographic film is positioned on the remote side of the crystal to receive and record the diffracted X-rays by transmission. The resultant photograph has the appearance of a number of spots. The fundamental Bragg formula $n\lambda = 2d \sin \theta$ is still fulfilled since the numerous crystallographic

planes each diffract that wave-length of the heterogenous beam for which the law is maintained. Fig. 32 (VII *) is a reproduction of a typical Laue photograph (of wernerite).

When the incident X-rays are parallel to one of the principal axes of the crystal, the resulting photograph reveals the symmetry around that axis, or the pseudo-symmetry of the crystal. By the use of gnomonic projection [1] method, indices may be assigned to each spot, but the deduction of the crystal structure by this method is a complex process, chiefly because the relative intensity of the spots on which deductions of structure are largely based, is not only dependent on the diffracting crystallographic planes but also on the intensity of the diffracted wave-lengths. Remarkable success with the method has been achieved by Wyckoff.
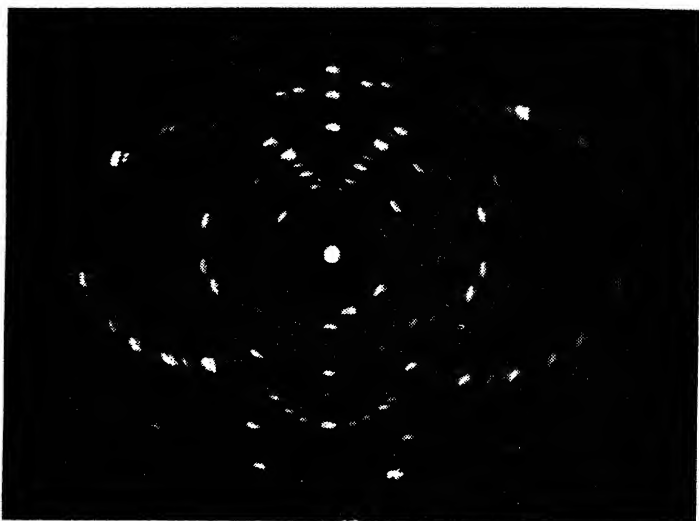
FIG. 32 (VII *)

Bragg Method. In this method monochromatic radiation reflected from a single set of planes of a crystal either set at the diffraction angle or oscillated over a small angular range including the diffraction angle, are recorded on a suitably disposed photographic film or by an ionization chamber. The schematic arrangement of the method is shown in Fig. 33 (VII *). Monochromatic radiation from the X-ray tube A, passes through the slit system D, D', and is diffracted by the crystal at E. The diffracted beam is then recorded by an ionization chamber G or photographic film H. In order to set the crystal at the diffraction angle, it is mounted in a holder contained in a graduated table. When the crystal is set at the centre of the circle made by slit system and photographic film, it will be seen that by geometry, the rays diffracted by a relatively large area of the crystal become focused to the slit width at the film. The method permits of accurate determinations of the spacing of the planes, and also

[1] Wyckoff, *The Structure of Crystals.*

has the important advantage that relative intensities of the recorded diffractions are directly comparable. Nevertheless the necessity of separate settings to record the reflections of each of the planes in turn seriously limits the scope of the method. It is now rarely used except in the case of complex structures where the accuracy of measurement and intensity ratios are of very considerable importance.

Debye-Scherrer Method. This method, also independently developed by Hull at the same time, overcomes the main difficulty of the Bragg method. Monochromatic radiation, defined by suitable slits, is diffracted by the specimen in the form of a fine disordered mass of crystalline powder, situated at the centre of a cylindrical camera on whose circumference is the photographic film and slit system. In the disordered mass, there must always be groups of crystals with their (100) planes properly orientated for diffraction to occur, and so with other planes. Therefore, the powder being at the centre of a camera on whose circumference both the slit system and photographic films are contained, the focusing effect, which permits of accurate measurement, is retained and one exposure only is necessary to secure the reflections of the monochromatic beam from all crystallographic planes.

FIG. 33 (VII *)

The powder may be adhesed to a hair, or other thin material whose structural pattern will not mask or be confused with that of the specimen.

In powders which are too coarse the section of complete diffracted cone of rays recorded on the photographic film, will be replaced by a series of spots on the cone, and to remove this effect the specimen may be rotated. Although the method permits of high accuracy of spacing measurements, the identification of the lines can be achieved only by finding by trial and error a Unit cell which will give the same spacings. The method is therefore useful only for those structures in which the variable factor, i.e. the length of the unit cube, is one—i.e. cube system. By the use of graphs constructed by Hull it is possible to assign values to lines of the hexagonal class of crystal.

Nevertheless, when used within its range of usefulness, i.e. crystals of cubic system, the method is one of very great value. It is claimed by Bradley and Jay [1] that spacing measurements of well-annealed metallic specimens may be made to 1 part in 40,000. Relative intensities of the lines are comparable and from them the atomic arrangement within the crystal may be determined. Since with this method low order reflections
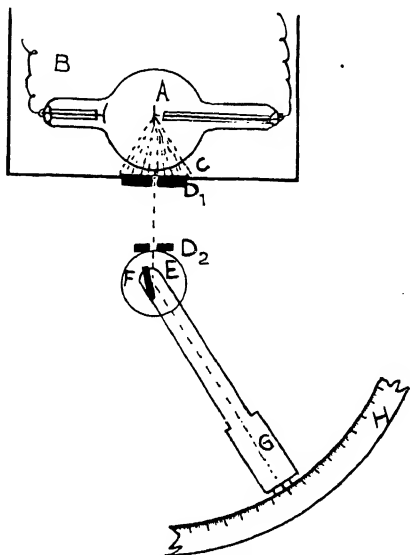
[1] Bradley and Jay, *Proc. Phys. Soc.*, 1933, 45, 507–22.

are also recorded, the method yields valuable information on the super-
lattice structures in metals and alloys, caused by order-disorder changes.

The Rotation-Single Crystal Method. In the Laue method of analysis
the crystal was set at a definite orientation and made to diffract a hetero-
geneous X-ray beam. In this method, due to Schiebold and Polanyi, a
single crystal rotated about an axis perpendicular to the beam is bathed
in a beam of monochromatic radiation. The diffracted beams are recorded,
most usually, on a cylindrical photographic film whose centre is the rotating
crystal. Complete rotation of the crystal is not essential, and oscillation
over a small range will suffice. Interpretations of the result are more
difficult than with the Laue photograph, since the orientation of the crystal
giving rise to a spectral reflection is unknown. The feature of the rotation
photograph is, however, that when the crystal is set with an important
axis perpendicular to the X-ray beam, the resultant photograph is a series
of spots on a series of layer lines. Now since one of the principal axes of
the crystal has been set parallel to the axis of rotation, all planes parallel
to that axis will in turn diffract the monochromatic beam, in the rotation
of the specimen, horizontally. For example, if a crystal be set with its
' 0 ' axis parallel to the axis of rotation, all planes of the rotation $0kl$ will
diffract from the X-ray beam horizontally, to form the zero layer line.
Those of the rotation $1Kl$ will form the first layer line, those of the rotation
$2Kl$ will form the second line, and so on. In the case of cubic crystals,
when one of the axes is parallel to the axis of rotation, another must be
perpendicular to it, and therefore spots will also form on similar layer lines
in a perpendicular direction.

The distance between the layer lines·is a direct function of the spacing
along the axis of rotation, and may therefore be readily calculated. The
assigning of indices to the spots is, however, a matter of great difficulty
since the angular orientation of the crystal in producing the diffraction is
unknown. Nevertheless, the method is of great value and enables the space-
lattice and space-group to be readily deduced.

Weissenberg Method. This method is similar to the single crystal
rotation method, in that a rotating single crystal set with a principal axis
parallel to the axis of rotation is bathed in a monochromatic X-ray beam.
It differs from the former method, however, in that the photographic film
is shielded such that it can record but one layer line at a time, and in that
it is geared to the rotating crystal. Thus as the crystal rotates the film
rotates with it and therefore the position of the crystal causing each diffrac-
tion spot may be readily deduced. Thus whilst the indexing of each diffrac-
tion spot becomes a simple task, each layer line must be investigated in
turn. Fig. 34 (VII *) shows a single crystal rotation photograph of stearic
acid.

With the exception of the Weissenberg method all the above methods
of analysis are available on the E404 model of the Dr. Müller's improved
Goniometer X-ray Spectrograph, manufactured by Messrs. Adam Hilger, Ltd.

Hahn [1] describes a new form of X-ray diffraction apparatus for powders.
A beam of X-rays is defined by a suitable slit system so that it has the form
of the surface of a right circular cone. This beam falls upon the powdered

[1] *Rev. Sci. Inst.*, 1931, 2.

sample arranged in the form of a circle placed at right angles to the axis of the cone, with the centre of the circle lying on the axis. Thus for each point on the circumference of this circle diffracted rays spread out along the surfaces of right circular cones, the axes of which lie in the conical surface of the primary X-ray beam. These diffracted cones of a given angle 2θ will all intersect the axis of the primary X-ray beam at a single point, X, the location of this point being a function of θ, λ, and the constants of the apparatus. A flat strip of duplitized film placed along the axis will thus record the positions of all such points which result from the various values of θ and λ (cf. the Bragg equation $n\lambda = 2D \sin \theta$), the trace on the film occurring at two intersecting straight lines with a comparatively intense spot at the point of intersection.

FIG. 34 (VII *)

The slit system used consists of a brass cylinder, approximately 5 cm. in diameter and 10 cm. in length, with a conical hole along the axis, the diameter at the larger end being 4 cm. and the angle 11°. Into the outer cone fits an accurately machined conical brass plug, supported coaxially by cross members at both ends. The inner cone is slightly shorter than the outer, and one of the two supporting stems is threaded so that by rotating the inner cone the width of the slit can be adjusted to any desired value. The powder is placed in an annular slit milled in a circular brass sheet and is covered with cellophane. The film is held in a special film holder open on both sides and supported so as to be exactly along the axis of the two cones. The tube used is a water-cooled molybdenum target hot cathode tube.

The time required to produce a readable diffraction by this method should be less than that in other methods in common use at the present because a larger volume of sample is used to form the pattern and because the weak spots are formed nearer the sample.
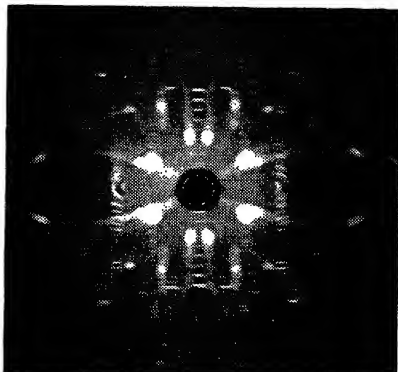
SECTION 6: THE SPECTROGRAPH AND CRYSTAL STRUCTURE

The interpretation of the results obtained will be best understood by reference to particular cases. The crystals selected are sylvine, rock salt, and zinc-blende, whose structures were amongst the first to be worked out by Bragg.[1] Rock salt is of particular importance as crystals of this substance are largely used as 'reflectors', when studying X-ray spectra. In Fig. 35 (VII *) the full lines AA represent crystal planes entirely composed
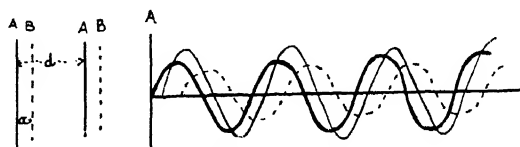

FIG. 35 (VII *)

of atoms of one element and the dotted lines BB represent planes of atoms of another element. The reflected train of waves from the B planes will then be out of phase with the reflected train from the A plane as shown. The resultant wave (not to scale) is shown in the light continuous line. If the spacing, or distance apart, of the A planes or B planes be d and the spacing of an A and a B plane be x, the phase difference of the reflected trains will be $\dfrac{2\pi x}{d}$ for first-order reflections, $\dfrac{2\pi(2x)}{d}$ for second-order reflections, and so on. The two trains reinforce one another for reflections of the nth order if $\dfrac{2\pi(nx)}{d} = K\dfrac{\pi}{2}$, where K is an odd number, and tend to destroy one another if $\dfrac{2\pi(nx)}{d} = K^1\dfrac{\pi}{2}$, where K^1 is an even number.

Fig. 36 (VII *) is a diagrammatic representation of first, second, and third order reflections from the three principal planes of sylvine and rock
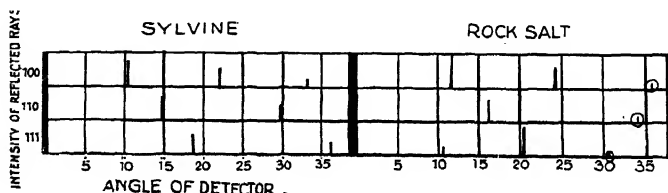
FIG. 36 (VII *)

salt, two crystals which belong to the cubic system. For the {100} planes of sylvine the glancing angle for the first-order reflection is 5·22°, and for

[1] *Phil. Mag.*, 1919 (6), *37*, 601; *38*, 639; *38*, 647.

rock salt $5\cdot9°$. This gives for sylvine $2d_1 \sin 5\cdot22° = \lambda$ or $d_1 = 5\cdot48\lambda$, and for rock salt $d_2 = 4\cdot85\lambda$, where d_1 and d_2 are the spacings of the {100} planes of sylvine and rock salt respectively. The sylvine crystal is built on the larger scale according to the relations

$$\frac{d_1{}^3}{d_2{}^3} = \frac{\text{mol. vol. sylvine}}{\text{mol. vol. rock salt}} = \frac{\dfrac{M_1}{\rho_1}}{\dfrac{M_2}{\rho_2}}$$

where M_1 and M_2 are the molecular weights of sylvine and rock salt respectively, and ρ_1 and ρ_2 their specific gravities. The number of atoms of metal and halogen associated with unit cube in each case is $d\sqrt[3]{\dfrac{\rho}{M}}$, which for sylvine $= 1\cdot63\lambda$, and for rock salt $= 1\cdot62\lambda$, so that the structure of both is analogous.

For sylvine we have

$$\frac{1}{d_{(100)}} : \frac{1}{d_{(110)}} : \frac{1}{d_{(111)}} = \sin 5\cdot22° : \sin 7\cdot30° : \sin 9\cdot05°$$

$$= 1 : \sqrt{2} : \sqrt{3}$$

whereas for rock salt the ratio works out as $1 : \sqrt{2} : \dfrac{\sqrt{3}}{2}$. These results assign to sylvine a simple cube lattice and to rock salt a face-centred cube lattice, whereas the formula $d\sqrt[3]{\dfrac{\rho}{M}}$ above points to similar structures. Furthermore, of the homologous series KCl, KBr, KI, and NaCl only in the case of the first does the intensity of the reflected ray diminish regularly for all three planes as spectra of a high order are reached (see Fig. 36 (VII*)).

In the case of the other three it is found that for the {111} planes we obtain a weak first reflection, a strong second, a very weak third, and a perceptible fourth. Bearing this in mind, a face-centred cube lattice may be assigned to the series as shown in Fig. 37 (VII *), the black spheres representing atoms of metal arranged on a face-centred cube, and white spheres representing atoms of halogen arranged on another face-centred cube, the two lattices intersecting as shown.

With this arrangement it is clear that both the {100} and {110} planes consist of both metal and halogen atoms, and so we

FIG. 37 (VII *)

obtain reflection of gradually decreasing intensity. The {111} planes however consist of alternate planes of metal atoms and halogen atoms evenly spaced, and if we now assume that atoms and not molecules are the diffracting centres, and it is clear that the reflections from the halogen planes are out of phase with those from the metal planes for reflections of the odd series, and
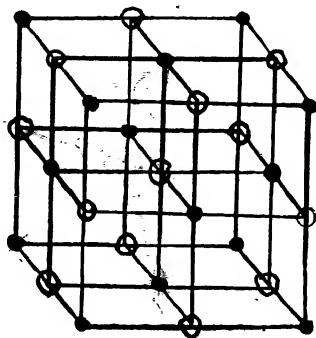
in phase for reflections of the even series. Remembering that the scatter-ing power of an atom for X-rays is proportional to its atomic weight, the amplitude of the wave reflected from the potassium planes (at. wt. $= 39$) is, within the limits of experimental error, equal to that of the reflections from the chlorine planes (at. wt. $= 35 \cdot 5$), and so in the case of sylvine the odd order reflections are entirely damped out with the result that the spacing obtained for the $\{111\}$ planes of sylvine is the spacing between a potassium and a chlorine plane and not the spacing between two potassium or two chlorine planes. In the cases of the other members of the series of salts mentioned the odd order reflections are only diminished in intensity as the amplitudes of the two reflected trains are unequal.

One other binary compound which crystallizes in the cubic system, and which exhibits some points of interest, is zincblende (ZnS). Its spectra for the three principal planes are shown diagrammatically in Fig. 38 (VII *). The positions of the first-order reflections are relatively the same as for rock salt, and it is found that

$$\frac{1}{d_{\{100\}}} : \frac{1}{d_{\{110\}}} : \frac{1}{d_{\{111\}}} :: 1 : \sqrt{2} : \frac{\sqrt{3}}{2} .$$

which shows that the crystal is built on a face-centred cube lattice. Also the molecular weight of zincblende is 97, its specific gravity is $4 \cdot 06$, and the first-order reflection from its $\{100\}$ planes is at $6° \ 10'$ so that

$$d \sqrt[3]{\frac{\rho}{M}} = \frac{\lambda}{2 \sin 6° \ 10'} \times \sqrt[3]{\frac{4 \cdot 06}{97}} = 1 \cdot 64\lambda.$$

so that there are the same number of zinc and sulphur atoms associated with unit cube as there are sodium and chlorine atoms in the case of rock salt. The two structures, however, cannot be alike, as it is only in the case of the $\{110\}$ planes that the intensities of the reflected beams diminish regularly. These planes therefore must contain both zinc (at. wt. $= 65$)
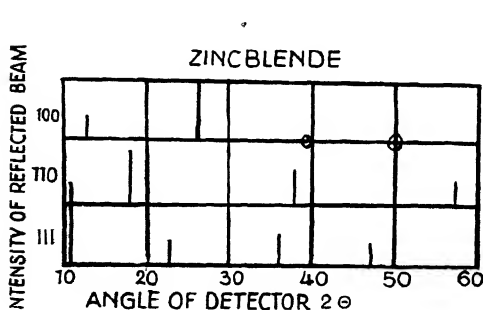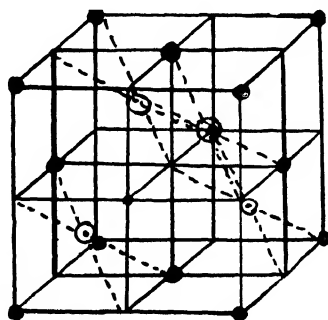

FIG. 38 (VII *)   • FIG. 39 (VII *)

and sulphur (at. wt. $= 32$) atoms. Since the structure underlying the crystal is the face-centred cube lattice the zinc atoms may now be arranged on such a lattice as shown by the black spheres in Fig. 39 (VII *). The sulphur atoms will likewise be arranged on a similar lattice, the two being then interlaced in such a manner as the observed spectra demand. The $\{100\}$ planes show a spectrum similar to that of the $\{111\}$ planes of rock salt

(Fig. 36 (VII *)) so that in these planes zinc and sulphur planes alternate at equal distances. In order to fulfil these two conditions, viz. that the {110} planes shall contain both zinc and sulphur atoms and the {100} planes alternate with equally spaced planes of zinc atoms and sulphur atoms, we must assign a structure such as that shown in Fig. 39 (VII *), where the sulphur atoms are placed at the centres of the small elementary cubes of which the unit contains eight. The {111} planes now contain alternately zinc and sulphur atoms, but the distance between a zinc and a sulphur plane is only $\frac{1}{4}$ that between two zinc and two sulphur planes. Referring to Fig. 35 (VII *), it is clear that reinforcement takes place for values of n that make $\frac{2\pi(nl)}{4}$ = an odd multiple of $\frac{\pi}{2}$, i.e. for the odd series, and damping for the even series. The spectrum for the {111} planes shows the odd series strong, and the even series weak, which confirms the structure assigned. It is interesting to note that should a crystal of zincblende develop the {111} faces one of the developed faces would contain sulphur atoms and the other zinc atoms. It is found that when such faces are developed by the crystal one is slightly larger than the other and behaves differently to solvents.

The absolute spacing of the various planes and the wave-length of the radiation used can now be determined on the assumption that the mass of the hydrogen atom is 1.64×10^{-24} grams. If we consider one of the face-centred cubes on which the sodium atoms, for instance, are arranged, we can make the following deductions. Each cube has eight corners, each corner being common to eight cubes, so that each cube has one corner associated with it. For each cube there are six points at the face-centres and each of these is associated with two cubes, so that the number associated with each cube is three. In all there are four atoms of sodium associated with each cube, or since each face-centred cube is divided into eight elementary cubes there is half an atom of sodium associated with each elementary cube and similarly half an atom of chlorine. With each elementary cube there is therefore associated half a molecule of sodium chloride. If M be the molecular weight of sodium chloride and m the mass of the hydrogen atom, the mass associated with each elementary cube is $\frac{Mm}{2}$. The volume of such a cube is $d^3_{\{100\}}$, and if ρ be the density of rock salt the mass of this cube is $d^3_{\{100\}}\rho$,

$$\therefore d^3_{\{100\}}\rho = \frac{Mm}{2}$$

For sodium chloride M = 58.5, ρ = 2.17, and m = 1.64×10^{-24},

$$\therefore d^3_{\{100\}} = \frac{58.5 \times 1.64 \times 10^{-24}}{2 \times 2.17}$$

which gives $d_{\{100\}}$ = 2.80×10^{-8} cm., and hence

$$\lambda = 2d \sin 5.75° = 0.576 \times 10^{-8} \text{ cm.}$$

for the palladium rays used by Bragg.

Much work on the structure of crystals has also been done by Debye and Scherrer, Hull and others, as a result of which it has been shown that in

any homologous series of salts such as the halides of the alkali metals or their rhombic permanganates the spacing of the planes increases with the atomic weight of the metal. Müller, in an investigation of the crystalline structure of the fatty acids from capric to behenic, found that the spacing increased with the number of CH_2 groups present.[1]

X-ray Spectrography. Once Bragg had demonstrated how the crystal grating could be used to reflect X-rays, a new avenue to chemical analysis had been opened up. Barkla and Sadler [2] had shown that different substances when bombarded by X-rays from a target of higher atomic number emitted secondary X-rays which were characteristic of the substances. Later, Kaye [3] and Whiddington proved that in order to excite this characteristic radiation it was only necessary to use the substance as the anti-cathode of the X-ray tube and regulate the voltage so as to generate sufficiently fast cathode particles. These characteristic radiations were first detected by measuring their hardness or power of penetrating aluminium, but a method has now been devised whereby their wave-lengths can be measured and compared. The substance to be examined is used as the anti-cathode of the tube, the rays emitted being then reflected by a crystal of known structure. From the values obtained for the glancing angles the wave-lengths of the various rays can be calculated from the equation $\lambda = 2d \sin \theta$, where θ is the angle for first-order reflections, and d is already known. Fig. 40 (VII *) shows photographs of the spectra of copper, platinum and mercury taken with the Müller spectrograph. A Shearer tube is supplied with an anti-cathode to the surface of which various substances can be affixed for spectrographic analysis.

Moseley [4] has shown that the relation between the spectra of different elements is simpler in the case of X-rays than in the case of visible light rays. He found that the characteristic radiation was of two types, one, which he called the K series, being of a distinctly harder quality than the other, which is known as the L series. Others working with vacuum instruments have detected the presence of a still softer radiation known as the M series. He further showed that each type consisted of three or more lines and that a distinct gap occurred between the K and L types of radiation. The different lines in any type were designated by the suffixes α, β, and γ, the line of longest wave-length in each series being known as the α line, and the others in order of wave-length as the β and γ lines. In both the K and the L series the α line was also found to be the most intense. Moseley afterwards showed that each of these lines was not a single line but a very close doublet resembling the D line in the luminous spectrum of sodium. The actual wave-lengths of both the $K\alpha_1$ and $K\alpha_2$ lines in this doublet were measured by Siegbahn in the case of some elements with the aid of his precision spectrographs. Mosely has also shown that as the atomic weight of the element rises the wave-lengths of the spectral lines decrease. The X-ray spectra of the elements are therefore much simpler than the light spectra and instead of consisting of an irregular number of irregularly spaced lines they consist—at least in the case of the heavier elements from aluminium up—of two or three sets of three or more lines each, the wave-

[1] *J. Chem. Soc.*, 1923, *123*, 2043.   [2] *Phil. Mag.*, 1908 (6), *16*, 550.
[3] *Phil. Trans.*, 1909, A, *209*, 123.   [4] *Phil. Mag.*, 1913 (6), *26*, 1024.

length of every line in every set decreasing with increasing atomic weight. This simplicity of X-ray spectra is very convenient in analytical work. By using an anti-cathode of the material to be analysed and a crystal of rock salt, the spacing of whose principal planes has been very accurately measured, it is possible to obtain photographs like those shown in Fig. 40 (VII *), in which the principal lines in the K or L series are obtained. A simple calculation made from the positions of these lines then gives the wave-lengths of the radiations to which they correspond and reference to a table of wave-lengths [1] enables us at once to name the element or elements present in the anti-cathode or in the powder for analysis which has been affixed to the special anti-cathode supplied. In this same paper Moseley has investigated the effects of the presence of impurities and has shown that the presence of 0·8 per cent Fe in a sample of cobalt gave the iron lines very strongly after an exposure of 5 minutes. In another experiment he
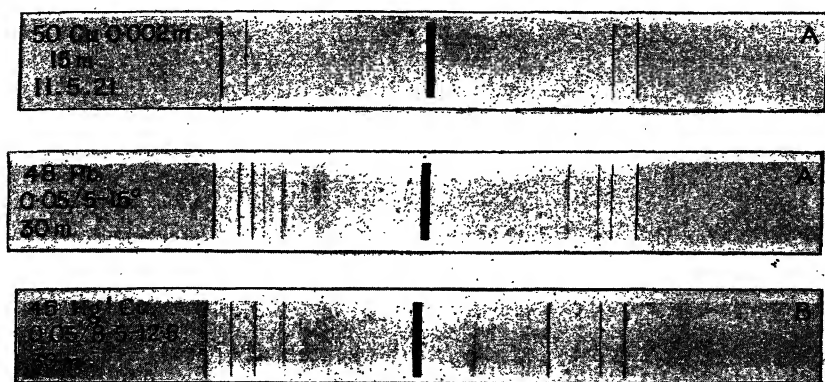
FIG. 40 (VII *)

showed that 2·2 per cent Mn in a sample of Ni showed the Mn lines, although only faintly. As a result of his work he came to the conclusion that 'the close similarity between X-ray spectra of different atoms shows that these are emitted by electrical charges within the atom near the nucleus and have no connection with complicated light spectra or chemical properties which are generated by electrons at the periphery of the atom'. In a later paper [2] he showed that a simple relation existed between the atomic number of the element and the frequency of any line in its X-ray spectrum. Thus, for a given type of line he found that $v = A(N - b)^2$, where v is the frequency of the line, N the atomic number, and A and b are constants for a given type of line. For the Kα lines $A = \left(\dfrac{1}{1^2} - \dfrac{1}{2^2}\right)v_0$ $b = 1$, and for the Lα lines $A = \left(\dfrac{1}{2^2} - \dfrac{1}{3^2}\right)v_0$ and $b = 7\cdot4$ where v_0 is the

[1] A table of X-ray wave-lengths will be found in Glazebrook's *Dict. of Applied Physics*, vol. IV, p. 603.
[2] *Phil. Mag.*, 1914 (6), *27*, 703.

fundamental Rydberg frequency. As a result of more accurate measurements with his precision instruments Siegbahn [1] showed that the relation is not quite so simple as Moseley believed. The relations obtained by Moseley and quoted above were obtained as a result of a systematic investigation of the X-ray spectra of many elements. During this investigation he found that the light elements like sodium and magnesium gave complicated spectra, but that the spectra of the heavier elements from Al up were simple. He found that the graph of atomic number against the square root of the frequencies of any of the spectral lines was a straight line, a result which enabled him to forecast the existence of missing elements of atomic numbers 43, 61, and 75, situated between Mo and Ru, Nd and Sa, and W and Os respectively. It is the irony of fate that the presence of the first element discovered by the aid of its X-ray spectrum (Haffnium,[2] At. No. 72) was not foretold by Moseley. He missed its position by assigning to Thulium (Tm) two positions for reasons which he explains. Haffnium was discovered by Coster and Hevesey during an X-ray investigation of extractions of zirconium minerals. They estimated the amount by adding known proportions of other elements present, and comparing the intensities of the haffnium lines before and after the addition.

The remarkable relationship between the frequencies of the spectral lines and the atomic number of the element giving rise to them has already been commented upon. Siegbahn has made extremely accurate measurements of the wave-lengths of certain lines with the object of confirming (or otherwise) the theoretical investigations of Vegard,[3] Kroo, Sommerfeld,[4] and others on the constitution of the atom. Some details of these theories and their results as mathematically deduced will be found in the publications mentioned.

Soft X-rays.[5] X-ray spectrography was formerly based exclusively on the use of crystal gratings. It is supposed that the atoms in crystals are regularly arranged in ' space lattice planes ', of which the distance apart d— the constant of the grating—was calculated by means of certain hypotheses due to Bragg. It was very desirable to obtain a standard measure of the wave-length of X-rays, by substituting a ruled grating for the crystal grating.

Moreover, the extension of spectrographic work in which a crystal was used for the study of the very soft X-rays met with great difficulties arising from the necessity of finding crystals with a spacing of nearly 100 Å, and from the great absorption of soft X-rays in the interior of the crystal, which causes error in the measurement of wave-lengths.

For all these reasons it was necessary to effect the diffraction of X-rays by mechanically ruled gratings. One apparently insuperable difficulty presented itself : the insufficient number of lines that could be ruled to a unit of length and consequently the too limited dispersive power for waves as short as X-rays. It is possible, however, to avoid this difficulty by

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[1] *Phil. Mag.*, 1919 (6), *37*, 601.

[2] Coster and Hevesey, *Nature*, 1923, *111*, 79, 182, 218, 252.

[3] *Phil. Mag.*, 1918 (6), *35*, 293 ; *idem*, 1919 (6), *37*, 237.

[4] *Atomic Structure and Spectral Lines* (Sommerfeld).

[5] The data on Dr. Thibaud's X-ray spectrograph was supplied by Messrs. A. Hilger, Ltd. (London), who give permission for use. They also kindly supplied blocks for related diagrams.

directing the rays which are to be analysed on to the surface of the plane grating, not in the usual way, but almost tangentially. Under these conditions the effect on the incident wave is as if the lines of the grating were much nearer together. In the case of the tangential grating one may express the classic grating formula as follows:

$$n\lambda = \frac{d}{2}\Delta\alpha \qquad (1)$$

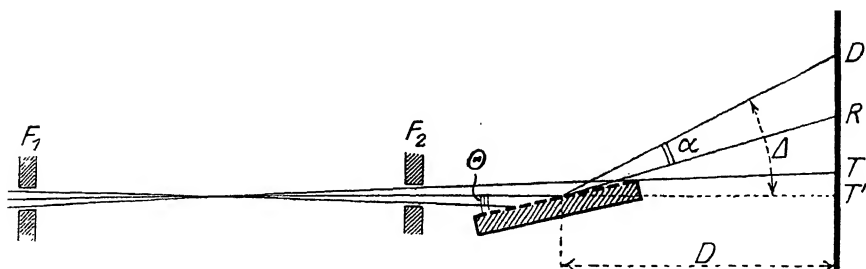where d is the distance from line to line of the grating (Fig. 41 (VII *)).

FIG. 41 (VII *)

For values of θ—the angle with the surface—of the order 10^{-3}, the dispersion of the grating is increased and it becomes possible to diffract the ordinary X-rays with an appreciable angle α even with a grating of 50 lines per millimetre. As the refractive index for the rays is very slightly less than unity $(1 - 10^{-6})$, the use of a very small angle θ, less than the limiting angle of total reflexion θ_m, makes it possible to arrive at conditions where there is total reflexion of radiation on the surface of the grating, which fact considerably increases the intensity of the diffracted rays. Fig. 42 (VII *) shows a spectrum

FIG. 42 (VII *)

of the extreme ultra-violet (copper spark). (Grating with 200 lines per millimetre.)
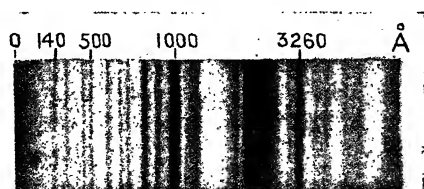
Dr. J. Thibaud was the first to show that it is of interest to apply the same technique to those spectral regions for which spectrographic apparatus is lacking, and more particularly to the radiations between the X-rays and the extreme ultra-violet.

Spectrograph. As X-rays of very long wave-length are extremely easily absorbed, the whole apparatus has to be placed in a chamber capable of being evacuated. This consists of a cylindrical brass tube AA, free from any leakage, 60 cm. in length and 18 cm. in diameter (Fig. 43 (VII *)). The vacuum is obtained either with a Holweck rotary molecular pump or with a multi-stage diffusion pump, in series with an oil pump to give the requisite fore-vacuum. A small lateral tube with two electrodes enables

one, by the appearance of its discharge, to estimate the degree of exhaustion. In this manner a good X-ray vacuum is very easily and quickly obtained.
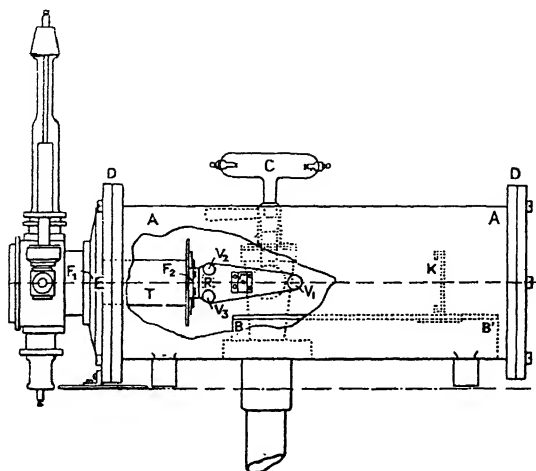

FIG. 43 (VII *)

Source of Radiation. This is detachable and is placed at the centre of one of the ends of the cylindrical tube. According to the results of the experiments mentioned, the source may be either a chamber with condensed spark for obtaining spark spectra of the extreme ultra-violet, or an X-ray tube with incandescent cathode for getting spectra in the soft X-ray region. The sparking chamber includes two electrodes, one earthed, the other insulated by a glass tube, both adjustable and provided with pincers. The current is taken from a battery of condensers of 0.02 μF, which is charged to 40 kilovolts by an X-ray transformer.

The X-ray tube, of metal and easily detachable, is particularly strong. The anode, which is interchangeable, is water-cooled; the cathode is incandescent. The tube is provided with water-circulation which cools the ground-in conical joints, which are all detachable and rendered vacuum-tight by rubber grease. The tube is charged to 1,000 to 2,000 volts by a small auxiliary dynamo and can take more than 150 milliamps. A ground-in conical metal fitting makes it possible easily to unite or separate the source and the spectrograph.

Grating. Two adjustable slits F allow a narrow pencil of rays from the anti-cathode (or from the spark) to fall tangentially on the grating. This grating is supported by a stand with three levelling screws, which facilitate adjustment. The grating is plane, ruled on glass with 500 to 1,000 lines per mm.[1] and the dimensions must not be too large (7 × 10 mm., for instance). The surface of the grating must be very carefully cleaned by washing with collodion.

It should be noted that in Dr. Thibaud's spectrograph the radiations do

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[1] A grating with 200 lines per mm. is very suitable. At the same time its dispersion is only half as much as that of a grating of 1,000 lines.

not have to pass through any *material screen* on the path from the source to the plate.

Photographic Plate. This is supported by a carrier which can be moved in a slide along the axis of the spectrograph, if it is desired to vary the dispersion. The plate may thus be placed in any position between 10 and 45 cm. from the grating.

Adjustment. (*a*) The axis of the two slits is adjusted by moving the second slit parallel with itself, so that the incandescent filament of the cathode does not enter the path of the useful rays. The slits can be adjusted to a size of 0·1 mm. on an average.

(*b*) It must be verified that the beam cut off by the two slits really strikes the active surface in the centre of the anti-cathode.

(*c*) Adjusting the grating. To do this, detach the arrangement carrying the grating and the slits and place this on the special stand in front of a mercury vapour lamp. By means of the three screws, bring the grating into such a position that the beam cut off by the two slits falls on it almost at a tangent. Adjust the angle of incidence (reckoned from the surface of the grating) to equal about 3×10^{-2} radians. Under these conditions, if one stands at the side, one should see the brilliant lines of the mercury arc spectrum in several orders appear on the surface of the grating. Adjust the screws very delicately to obtain the maximum degree of brightness of these lines.

The adjustment is final. It remains the same, at whatever distance one places the plate, and for the study of any wave-lengths.

Clean the surface of the grating from time to time with collodion.

Loading and unloading are very simply effected by placing the spectrograph in a dark room and cutting off the light at the moment the photographic plate is placed in position.

Finally, a small lateral tap enables one to introduce only air filtered and dried by a column of pumice which has been impregnated with sulphuric acid.

Dr. Thibaud's spectrograph, filling the gap between the X-rays and the ultra-violet, renders possible a large number of experiments, both *spectral* and *atomic*.

(*a*) Production and study by photographic record of the properties of very long wave X-rays and junction with the ultra-violet.

(*b*) Study of the *emission spectra of normal atoms* (low tension X-ray tube) between 10 and 100 Å. Exploration of the K and L series of the light elements and of the higher series (M, N, O . . .) of the heavy elements.

(*c*) Standard measurement of the wave-lengths of X-rays (calibrating the grating with a well-known line in the visible spectrum) whence, by comparison with the wave-length measurements made with a crystal, a determination of the dimensions of the space lattice of crystals. This last is of great importance, as it leads to new and precise estimations of *Avogadro's number* and of the *elementary charge of the electron*.

Recent Applications. There have been rapid developments in the study of X-ray spectroscopy, especially in its relation to crystal structure. X-ray analysis shows what the molecule in compounds is like and indicates the nature of the linkages between the atoms.

X-ray diffraction diagrams have been employed by Champetier and others in the study of the crystalline structure of cellulose and other fibres.[1] A special technique has developed in connexion with this type of work and it will be considered in the supplementary volume of *Physico-Chemical Methods*.

Another interesting application of X-ray spacing analysis deals with the determination of the structure of long chain compounds, e.g. the higher members of the fatty acid series. Some of the earlier work on this subject is due to Müller.[2] More recent application of the measurement of 001 crystal spacings of fatty acid and other constituents of natural waxes to the identification of these compounds has been worked out by Chibnall, Piper and others.[3] The structure of many aromatic compounds has also been investigated by the method of X-ray analysis. A number of references are given to some general and some special problems in connexion with crystal determination.[4] See also, Suggestions for Further Reading, p. 575.

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[1] *Ann. Chim.*, 1933, *20*, 5. A summary of the literature of the X-ray examination of cellulose and derivatives is given by Sisson, *Textile Res.*, 1934. See also Marsh and Wood, *Introduction to the Chemistry of Cellulose*, Chapman-Hall, 1938 (Chap. 21).

[2] *Proc. Roy. Soc.*, 1928, *A120*, 437; *ibid.*, 1929, *A124*, 317.

[3] *Biochem. J.*, 1931, *25*, 2095; *ibid.*, 1934, *48*, 2175.

[4] For further reading the following books and papers may be consulted:

Mee, *Physical Chemistry*, Heinemann, 1934 (Chap. 7).

Stilwell, *Crystal Chemistry*, McGraw-Hill, 1938.

Bradley, *Phil. Mag.*, 1924, *47*, 657. ('Structure of Metallic Arsenic,' a classical paper on crystal analysis by Debye-Scherrer method.)

Weissenberg, *Zeits. f. Phys.*, 1924, *23*, 229. (New Method of Analysis.)

Seljakow & Sons, *Zeits. f. Krist.*, 1934, *89*, 601. (Indexing of Rotation Photo.)

Seljakow, *Zeits. f. Phys.*, 1934, *92*, 543. (Relation between rotation photograph and stereographic projection.)

Congress Kolloidal Physics, *Koll. Phys.*, 1934, *69*, 264.

Bradley, *Proc. Phys. Soc.*, 1935, 879. (Absorptions by specimen in Powder and Rotation photographs.)

Straumains & Jevins, *Zeits. f. Phys.*, 1936, *98*, 461. (Precision Debye-Scherrer photographs.)

W. L. Bragg, *Nature*, 1936, *138*, 362. (Structure factor graphs.)

Tertsch, *Zeits. f. Krist.*, 1937, *98*, 275. (Axes of Symmetry.)

Laves, *Naturwiss*, 1937, *25*, 705. (Laue photographs.)

Conference on Conduction Electricity in Solids, *Proc. Phys. Soc.*, 1937, 49.

CHAPTER VIII *

ELECTRO-CHEMISTRY

SECTION 1: ANALYSIS AND PREPARATIONS

INTRODUCTION. The subject-matter included in the term electro-chemistry as generally understood is very wide, and in the present chapter only some typical methods can be considered.

Electro-chemical Methods. Electro-chemical methods can, like organic chemical methods, be divided into two broad groups—analysis and preparation. Some typical methods will be briefly considered.

ANALYSIS

Probably the most important method of electro-chemical analysis is that involving the deposition of copper from a solution of one of its salts, and such an operation will be considered as a typical example of the deposition of a metal from solution. A number of methods have been proposed to accomplish this, but only one—rapid deposition from sulphuric acid solutions—will be discussed here.

Deposition of Copper from Solution. A compound or alloy containing copper is dissolved in nitric acid or in water if soluble, and evaporated with concentrated sulphuric acid (15 ml. of 6 N. acid per gram of metal) until all nitric acid, if present, is removed. The whole is diluted to 300 ml. per gram of metal (0·3 gram is sufficient for the analysis), and the solution is electrolysed in the cold in a beaker with a platinum anode of the shape shown and a cathode which consists of a vertical cylinder of platinum gauze fastened to a vertical platinum wire which is rotated by an electric motor, at about 400 revolutions per minute (Fig. 1 (VIII *)). A current density of about 5 amps. per square decimetre, with an absolute current of 5 or 6 amps., is employed. Electrolysis of 1 gram of metal is complete in about 15 minutes; the end-point is determined by with-

To Motor

FIG. 1 (VIII *)

drawing a drop of the solution and mixing it on a white tile with a drop of potassium ferrocyanide solution, when no red cupric ferrocyanide is obtained.

341
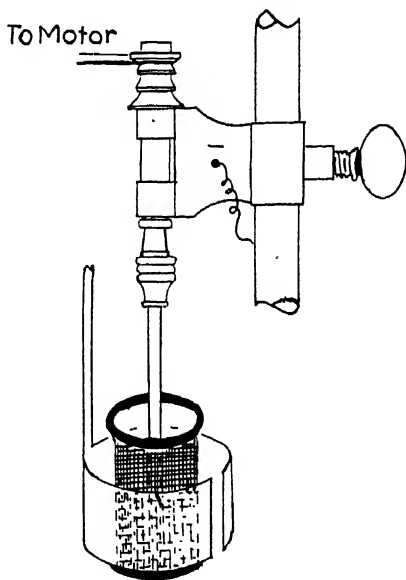
The platinum cathode, which has been weighed before the experiment, is washed in water and alcohol, dried at 100° in a drying oven, cooled in a desiccator, and weighed.

The above method can be employed to determine copper in a number of alloys and compounds. Under suitable conditions one metal can be deposited quantitatively in presence of others.

Removal of a Metalloid (Arsenic) from Solution. It is frequently necessary to determine traces of arsenic in foodstuffs and the like, and for this purpose the method described below is often employed.

The method consists in the electrolytic formation of hydrogen in the presence of the material containing arsenic compounds with the resulting formation of hydrogen arsenide. This gaseous product is swept out of the reacting vessel with the excess hydrogen, and on passing through a heated tube is decomposed and arsenic deposited as a characteristic
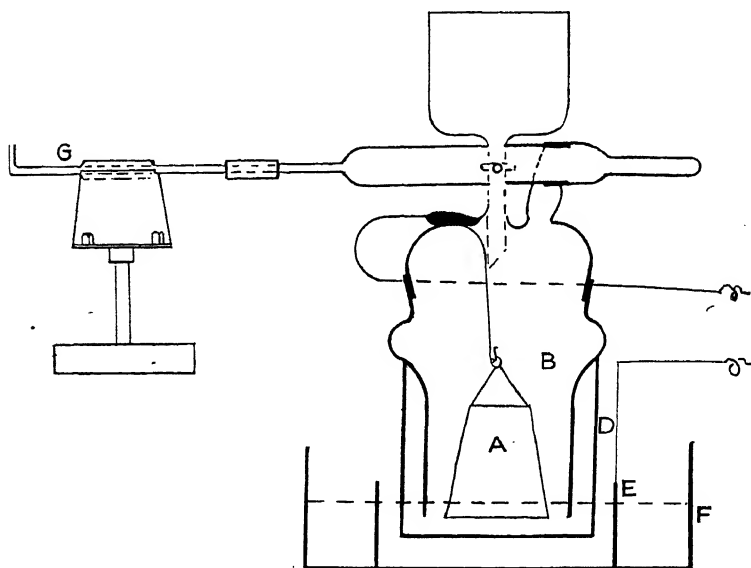
FIG. 2 (VIII *)

mirror. The amount of arsenic is estimated from a comparison with mirrors formed from known amounts of arsenious oxide similarly treated. The method is only suitable for the estimation of traces.

Apparatus Employed. The arrangement of apparatus is shown in Fig. 2 (VIII *). It consists of a platinum electrode A which hangs in a glass vessel B, which is provided with (i) a stopper funnel for the addition of the sample under test, (ii) gas exit tube, and (iii) other connexions as indicated. The vessel B is opened at the end and fits into a Pukal porous cell D, which constitutes the inner cell for the cathode, where the hydrogen and hydrogen arsenide are produced on the passage of the current. This cell is made of unglazed highly silicious ware and is from 1–1·5 mm. in thickness. It may be cleaned after repeated use by heating in a muffle furnace to burn off organic impurities. In Trotam's modification this cell is replaced by a parchment membrane.

The inner electrode, which is cone-shaped, forms the cathode and is made of sheet platinum with perforation. It is suspended as shown in the figure. The cell for the anode consists of a thick glass vessel E. The anode is a band of platinum 2 cm. broad, passing loosely around the porous cell and connected with the current supply by a thick platinum wire. The liquid in the vessel E is kept below 50° and the vessel F contains circulating water. In warm weather it is sometimes necessary to cool with ice. The upper portion of the vessel B is open and has a ground neck for the attachment of the drying tube, which contains anhydrous calcium chloride. To this tube is attached a capillary hard glass tube on which the arsenic is deposited.

Preparation of the Capillary Tube. A piece of glass tubing having an external diameter of 5 mm. and an internal diameter of 3·5 mm. is cleaned by successive treatment with acid, water and alcohol and then dried. It is then heated in the blowpipe flame so that a portion of the tube about 2 cm. in length and 5 cm. from the end of the tube is thoroughly softened, the heated portion is then drawn out to a length of 7 to 8 cm. and cut a distance of 1 cm. from the shoulder of the tube. The tube is cut off near the end (external diameter of 2 mm.) and it is turned at right angles about 1 cm. from end.

When the capillary tube is in position a piece of platinum gauze is wound round the tube at the portion where it is heated.

The apparatus constructed by Thorpe had an apparent resistance of 1·4 ohms, the potential difference between the ends of the wires of the poles being 7 volts with a current of 5 amps. This strength of current gave 40 ml. of hydrogen in one minute.

Method of Working. The cell D is filled with sulphuric acid (30 per cent). This acid is run into the porous cell by means of the funnel. The porous cell should be soaked in dilute sulphuric acid for half an hour before use. A current of 5 amps. is passed through the solution, and after ten minutes, when the apparatus is practically free from air, the issuing hydrogen is ignited and the Bunsen burner lighted. The heating of tube and passage of current is continued for fifteen to twenty minutes, and if no deposit (brown ring) is formed in tube G the reagents may be considered practically free from arsenic and suitable for use in the estimation of arsenic. The solution to be examined is then introduced. If a solid it is treated by the ordinary analytical methods so as to separate the arsenic compound present in a separate solution and this liquid run in. The current is continued for thirty minutes and the operation of heating the tube, &c. continued. The capillary is then sealed at both ends and the amount of mirror in the tube compared with standards previously prepared. The standard tubes correspond usually to 0·004, 0·006, 0·008, 0·01, 0·014 and 0·018 milligrams of arsenious oxide. These standards are prepared by adding known amounts of arsenious acid solution (strongest solution necessary to test will contain 0·1 gram of arsenious oxide in 1 litre of liquid) to the above apparatus and preparing the mirror as indicated.

Arsenates are not reduced in the above apparatus, and it is necessary with such compounds to treat first with nascent sulphur dioxide in solution before introducing into the electrolytic vessel. By the use

of lead electrodes this extra step is unnecessary, and in the apparatus of Sand and Hackford this property is utilized. Details of the apparatus (Fig. 3 (VIII *)) are as follows :

(A) Cooling vessel for water, conveniently replaced by an insulated lead trough, when several sets of this apparatus are being used simultaneously.

(B) Anode compartment.

(C) Anode of lead lid-shaped to minimize spraying of acid, with a slot to allow cathode to be observed. Height 5 inches, inner chamber 2 inches, bent inwards at the bottom to support the cathode compartment, the latter being conveniently placed on a glass-rod triangle (not shown in figure) to allow bubbles of oxygen to escape more readily.

(D) Cathode compartment, glass cylinder, width 1·625 inch, height 7 inches, closed at one end by an india-rubber stopper, at the other end by arsenic-free parchment paper, tied while wet by means of string and kept in its place by the flange on the end of the cylinder.

(E) Cathode of pure lead (arsenic-free confirmed by test), solid. Height 1 inch, thickness 0·75 inch. Length of stem 7 inches.
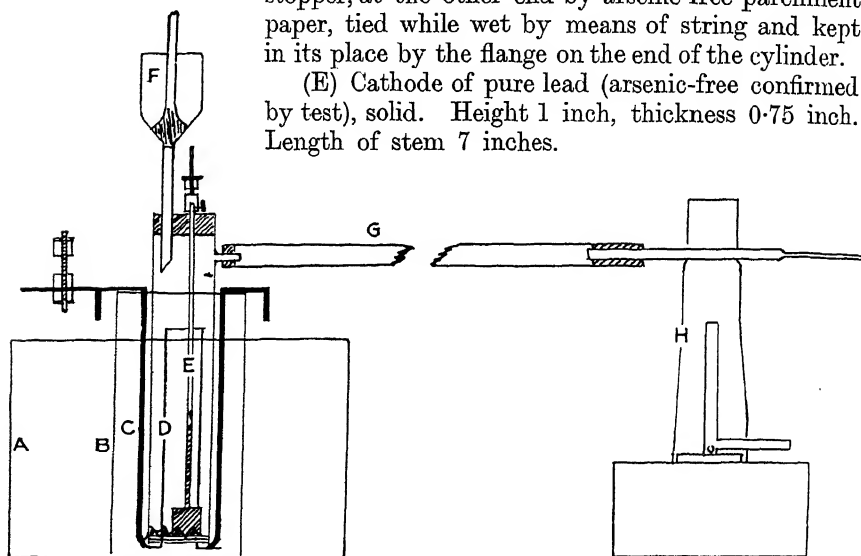
FIG. 3 (VIII *)

(F) Funnel, with wide stem, having graduations of 10 ml., 25 ml., 50 ml. and closed by a ground-glass rod.

(G) Drying tube charged with (a) lead acetate paper, (b) calcium chloride, and (c) plug of cotton wool.

(H) Shield to protect Bunsen burner from draughts.

Current : about 5–6 amps., that is, for a single apparatus 9–10 32-c.p. lamps on a 200-volt circuit.

Electrolyte : anode solution, 10 per cent sulphuric acid. Cathode solution : liquid under examination. Temperature, 15°–50°.

As an example of the use of the apparatus for the testing of arsenic in (a) malt and (b) beer the following details are given from the original paper :

(a) Forty grams of malt are thoroughly shaken in a beaker with 100 ml.

of a 10 per cent solution of sulphuric acid and heated on the water-bath for twenty minutes with occasional shaking, the beaker being covered and the temperature not being allowed to rise above 50°–60° in order to minimize evaporation. 50 ml. of the solution are then introduced into the apparatus, a few drops of amyl alcohol being added to prevent frothing. Half an hour is allowed for the total deposition of the arsenic.

(b) 10 ml. of strong sulphuric acid are added to 50 ml. of the beer and introduced into the apparatus, together with a few drops of amyl alcohol, half an hour being allowed for the deposition of the arsenic.

PREPARATIONS

A. Inorganic. Preparation of Potassium Persulphate. The apparatus shown in Fig. 4 (VIII *) is erected. It consists of a platinum basin of about 200 ml. capacity, which forms the anode, and a short platinum wire which is the cathode and a porous pot of the usual type. The basin is supported in a trough which can be heated or cooled. The basin is filled with a saturated solution of potassium hydrogen sulphate, while the porous pot contains dilute sulphuric acid. A current of 3–3·5 amps. is employed, and in the course of a few days potassium persulphate forms in the basin, hydrogen being evolved at the cathode. The salt is collected and dried on a porous plate, and is recrystallized from water.
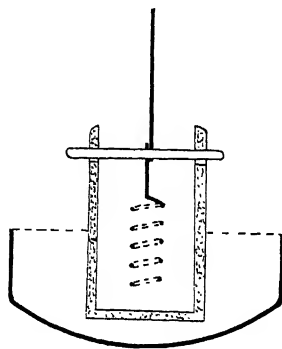
FIG. 4 (VIII *)

B. Synthesis of Organic Compounds. Preparation of Ethane. A porous pot is half-filled with a cold saturated solution of sodium acetate containing a little glacial acetic acid, and is fitted with a two-holed stopper through which passes a delivery tube, and a platinum wire to serve as an anode. The stopper after fixing is well painted with wax or with cellulose acetate dissolved in acetone. The pot is placed in a large beaker containing a similar solution of sodium acetate and a coiled platinum wire serves as a cathode. The whole is immersed in a bath of water which is kept below 20°. A current density of 60–80 amps. per square decimeter of anode surface is employed. The gas evolved at the anode is washed with concentrated potassium hydroxide solution to remove the carbon dioxide, which is evolved with the ethane at the anode.

Preparation of Diethyl Adipate. A saturated solution of potassium ethyl succinate (see below) is electrolysed in a tall beaker using a platinum wire as an anode; the cathode is a piece of platinum foil. A current density of 60–80 amps. per square decimetre of anode surface is employed; each 100 ml. of solution requires about 30 amp. hours. Considerable frothing occurs in the beaker, which must not be more than half full. No porous diaphragm is required. The liquid, when electrolysis is finished, is extracted with ether to remove the adipic ester which floats on the surface; the ethereal solution is dried over anhydrous calcium chloride,

the ether is removed on the water-bath and the residue distilled. Adipic ester passes over at 254°. Yield 30–35 per cent of the theoretical.

Potassium Ethyl Succinate is prepared by dissolving 1 molecular proportion of diethyl succinate in a concentrated alcoholic solution of 1 molecular proportion of potassium hydroxide. After four hours the whole is evaporated nearly to dryness on the water-bath in a current of carbon dioxide; water is added to dissolve the solid precipitate. Any unchanged diethyl succinate is extracted with ether and the concentrated solution obtained is used as described above.

A modern redesigned form of Sand's electro-chemical apparatus [1] appli-
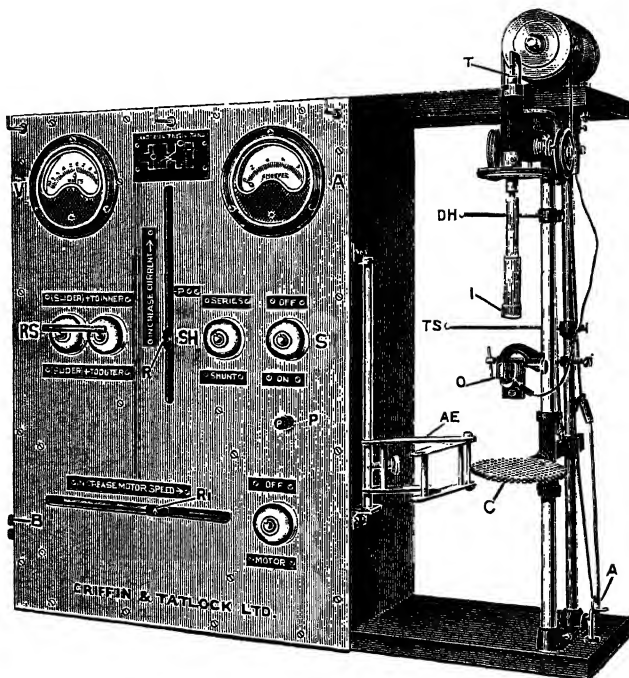
FIG. 5 (VIII *)
(Dimensions 31 × 9 × 27 inches.)

cable to electrolytic, potentiometric, and conductometric analysis and to pH measurement, may be mentioned.

This apparatus is designed primarily for electroanalysis and for the rapid separation of metals by graded potential, but it is equally suitable for ordinary electrolytic deposition and, by the use of accessories, it is applicable to potentiometric and conductometric analysis and also to potentiometric pH measurement. In addition, a convenient stirrer, capable of independent use, may be operated from the motor by means of the driving clutch incorporated in the apparatus.

The apparatus was originally described in *J. Chem. Soc.*, 1907, *91*, 374. Further improvements having been made,[1] the external form of the apparatus has now been designed on compact and convenient lines to ensure simplicity in operation.

The apparatus is illustrated in Fig. 5 (VIII *) and its wiring diagram in Fig. 6 (VIII *), the letters, where common, having the same significance in each figure.

The front panel is of insulating material and carries an ammeter A and a voltmeter V, which latter is recommended for indicating the power consumption across the electrodes. The main switch S is for breaking

FIG. 6 (VIII *)

the battery circuit. The shunt switch SH allows the rheostat R, of 15-amps. carrying capacity, to be placed in shunt with the battery B for separations by graded potential. The reversing switch RS allows the outer electrode to be made either the anode or the cathode.
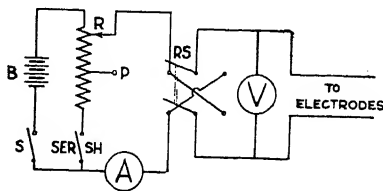
At the top of the stand a motor is mounted, controlled by a switch and by the rheostat R_1. The driving belt passes over two idle pulleys to a hollow shaft to which a short length of thick-walled rubber tube I is attached. The tube is closed at the lower end by a stainless steel rod secured to a V-grooved silver clutch and is filled with mercury which allows frictionless electrical contact with the inner electrode to be maintained. The outer (stationary) electrode is supported by the silver-lined clamp O and the inner (rotating) electrode, being provided with a silver rod at the upper end, is merely pushed into the silver clutch by which it is firmly held for rotation.

AE is an auxiliary electrode holder, universally adjustable; and for use in supporting the auxiliary electrode, Fig. 10 (VIII *), in analyses by graded potential.

The Electrodes. Fig. 7 (VIII *) shows the all-platinum electrodes (weight about 2 oz.) of the original design.[2] Owing to their high stirring efficiency these are very rapid, allowing the quantitative removal of about 0·25 gram. of copper in approximately 5 minutes.

FIG. 7 (VIII *)

Fig. 8 (VIII *), A, B and C, represent electrodes of the same general features but requiring a greatly decreased weight of platinum.[3] This is attained by mounting the inner electrode A on a glass support, connexion to the stand being made through a silver rod fixed to the glass by a lead seal. The outer electrode B is supported by the glass tripod C, which is held by the clamp O of the stand. A silver electrode similar to that illus-
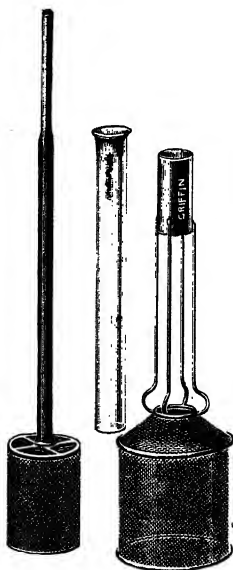
[1] *Analyst*, 1934, *59*, 328–38.   *Trans. Far. Soc.*, 1909, 5, 159.
[3] *Analyst*, 1934, *59*, 336.

trated in Fig. 8 (VIII *) B is available and is useful for zinc and for copper determinations.

Fig. 9 (VIII *) represents a type of anode which has frequently been found useful, e.g. for copper determinations in the presence of much iron.[1] It is intended for use when, in order to prevent oxidation, contact between the anode and the electrolyte to be analysed must be avoided. It is designed to allow a parchment thimble, slotted at the top, to be slipped over it from beneath and attached by thread. A revolving anode chamber is thus formed into which an electrolyte, such as acidified sodium sulphate or nitrate solution, may be poured through the funnel. Towards the end of a determination, this may be washed by fresh electrolyte into the cathode chamber so as to recover solute which has diffused into the anode chamber.
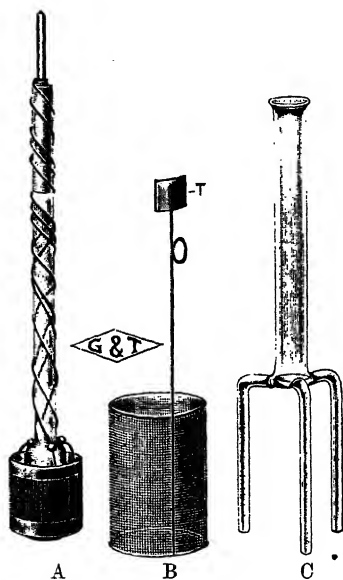
FIG. 8 (VIII *)   FIG. 9 (VIII *)

A stand with bottles containing alcohol and ether, respectively, has been found convenient for the rapid drying of electrodes.

The Auxiliary Electrode Vessel.[2] This vessel may be used as an auxiliary electrode in the separation of metals by graded potential and in potentiometric pH and other measurements. The design avoids defects noticed by Smith[3] in earlier types of vessel. The stem of the electrode is inserted into the auxiliary electrode holder AE (Fig. 5 (VIII *)). A copper lead passes from a terminal at the base of the stem to a platinum wire fused through the base of the body, thus making connexion with the mercury and electrolyte in the body and thence via the horizontal limb to the end of the vertical limb, which is so shaped as to minimize the entrance of

[1] *Analyst*, 1929, *54*, 277.   [2] *Ibid.*, 1934, *59*, 329.
[3] *Trans. Far. Soc.*, 1928, *24*, 216.

external electrolyte into the auxiliary electrode vessel. The bulb with tap is intended to hold a supply of the electrolyte (e.g. saturated potassium chloride solution) for flushing out the bent limb. The overall length of the vessel is about 16 inches.

The Potentiometer.[1] This may be used in potentiometric analysis or pH measurement. A dry battery is connected through fine and coarse adjustable rotary resistances which form the slide wire. The fall of potential along the slide wire is used to balance the pressure to be measured and a high resistance (50,000 ohms) voltmeter is then switched in to read the potential across the portion of the slide wire used for balancing. A switch is provided so that, if desired, the unknown potential may be connected direct to the voltmeter.

A feature of this method is that the voltmeter is used both as a graduated direct-reading instrument and also, by short-circuiting the series resistance incorporated in it, as a low-resistance galvanometer for use in balancing the potentiometer.

Hydrogen and Quinhydrone Electrodes. In potentiometric pH measurement Sand's Electro-chemical apparatus is very convenient, as the electrode

FIG. 10 (VIII *)

can be held in the outer electrode clamp O (Fig. 5 (VIII *)), and the auxiliary electrode is then immediately available in the special holder AE.

Fig. 11 (VIII *) illustrates a type of hydrogen electrode which has been found useful for routine pH determinations.[2] K is the cup for filling and
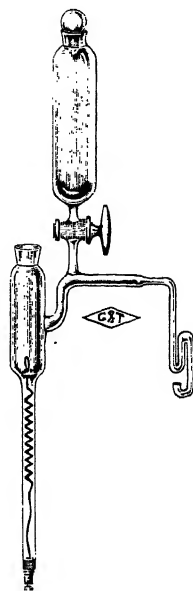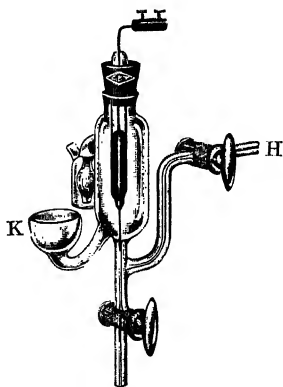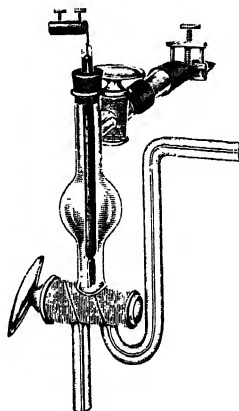

FIG. 11 (VIII *)

FIG. 12 (VIII *)

for entrance of the auxiliary electrode tip. Hydrogen enters by the tube H and escapes by the bubbler attached to the body of the electrode. A platinum wire with sealed mercury connexion is supplied.

Fig. 12 (VIII *) illustrates Sand's hydrogen electrode for use with small

[1] *Analyst*, 1934, 59, 331.   [2] Lindsey, *Analyst*, 1932, 52, 573.

quantities of liquid. A side tube with tap is provided for escaping hydrogen and a cylinder, sliding on this tube, is fitted so that potassium chloride (or other solution) may readily be drawn up the tube into contact with the hydrogen-saturated liquid. A two-way tap is fitted ; the bent tube from this is for hydrogen connexion and the straight tube to be dipped into a small dish containing the same electrolyte as the auxiliary electrode. The tip of the latter is also dipped into the electrolyte. A platinum wire with sealed mercury connexion is supplied.
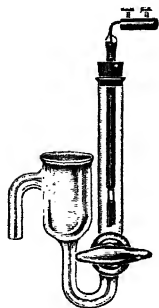
Fig. 13 (VIII *) illustrates a useful type of quinhydrone electrode. Into the left-hand limb the auxiliary electrode tip is placed. Electrolyte is then run in so that its junction with the test liquid in the right-hand limb is just at the top of the right-hand capillary. The stopcock assists in manipulation. A platinum electrode with sealed mercury connexion is supplied.

Fig. 14 (VIII *) illustrates a vessel for use in conductometric analysis. Its design follows closely on that described by Britton and German.[1] A glass container is provided with a ground-in ebonite stopper which is fitted with a fixed guide tube and with two platinum electrodes having sealed mercury connexions. The stem of a three-bladed stirrer is passed through the guide tube and is gripped by the inner electrode clutch I (Fig. 5 (VIII *)), while the guide tube is held in the outer electrode clamp O.
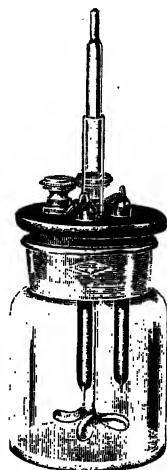
FIG. 13 (VIII *)

FIG. 14 (VIII *)

Assembling and Adjusting the Apparatus. Mercury is first poured through a capillary funnel into the tube T (Fig. 5 (VIII *)) (which makes connexion to the inner electrode) until it reaches to about 2 inches from the top. A few drops of machine oil are poured on the top of this. Connexions to the battery terminals B (10 amps. at 12 volts) and the motor plug (mains) having been made, the outer electrode clamp O must be set in position.

For use with the all-platinum electrodes (Fig. 7 (VIII *)), these are first assembled by pushing the glass guide tube through the collar and the upper ring of the outer electrode, the stem of the inner electrode being introduced into the guide tube from below. Connexion to the special chuck I (Fig. 5 (VIII *)), of the flexible rubber drive is then made by pushing the stem home between the silver contact piece and the rubber holder. The guide tube and outer electrode will now remain suspended and the clamp O is set in position in such a way as to grip the collar and guide tube, and at the same time allow the inner electrode to revolve freely, while it is enveloped on all sides, except the bottom, by the outer electrode.

The height of the support C is next adjusted. It is first lowered ; a beaker is pushed up from below so that its bottom almost touches the outer electrode and the ring C is raised to support it. The ring A on the leather

[1] J. Chem. Soc., 1930, 1250.

cord is then fastened to the hook on the base and the length of the cord adjusted by means of the special stop so as to be taut while holding the support in the position indicated.

To remove the electrodes from the stand, the support is lowered while the beaker is held in the left hand. The beaker is then removed, the clamp O loosened, and the inner electrode pulled out of its clutch. The assembly of electrodes and guide tube thus comes off together, and may be dismantled.

To adjust the stand for the glass frame pair of electrodes (Fig. 8 (VIII *)), the inner electrode A is inserted into the glass tripod C and suspended on the stand as in the case of the all-platinum electrodes. The outer electrode B is introduced from below, until its lower rim is flush with the bottom of the tripod legs. The clamp O is then made to grip, and at the same time make contact through its silver jaw with the tab T of the outer electrode.·

A **Simple Deposition**. The electrodes and beaker having been placed in position, the motor is switched on and adjusted to a speed of 250 to 300 r.p.m. by means of the horizontal slider, the vertical slider being placed at the lowest position.

In order to avoid loss of electrolyte by splashing during stirring, it is desirable to cover the beaker with a pair of cover glasses. These can conveniently be made from mica or bakelized paper by taking two rectangular pieces, each about 3×2 inches, and cutting in the centre of a long side of each and perpendicular to that side, a slot about $\frac{1}{2} \times \frac{3}{8}$ inch wide. The slotted plates can then be slipped on the stem of the outer electrode from opposite sides, and rest on the top of the beaker.

The solution is then heated to the required temperature, a thermometer having been suspended from the thermometer support TS provided and the main switch S closed. Care must be taken that the reversing switch RS has been set to its proper position, e.g. in a copper determination the outer electrode would be the cathode and in a lead determination would be the anode, lead being deposited as PbO_2 on the anode.

The shunt switch may be left open, i.e. the rheostat R connected in series. The current slider R is then raised until the ammeter gives the desired reading. Shortly before the end of the deposition, the cover glasses on the top of the beaker and the space between guide tube and stem of the inner electrode are washed with a jet of water from a supply bottle or from a wash-bottle.

In disconnecting, the beaker is gripped by its rim in the left hand, the support C being lowered from beneath it to its lowest position. A 5-inch evaporating-dish is placed upon the support and the beaker is then gradually lowered from the electrodes, the outer electrode being washed with a jet of water until it is outside the electrolyte. *Only now should the motor be stopped.* If desired, the washing may be continued with the electrode outside the electrolyte. The beaker is then removed, any drippings being caught by the dish. The outer electrode is now disconnected as already described and dipped into alcohol, shaken and then dipped into ether and dried. On no account must the current switch be turned off until the process of disconnecting has been completed.

Examples. (a) *Copper deposition* of about 0·25 gram of copper. Outer electrode cathode. Add 1 ml. of conc. sulphuric acid, 0·5 ml. of conc.

nitric acid, no external heating of electrolyte. Volume for glass frame electrodes, 55–60 ml.; current started at 4–7 amps. reduced to about half original value after blue colour of the solution had disappeared. Time, 15–20 minutes. For all-platinum electrodes vol. 70–80 ml., current started at 10 amps., later reduced to half original value. Time about 5 minutes.

A silver electrode of the form shown in Fig. 8 (VIII *) may be usefully employed in copper deposition. The copper is stripped after a deposition, by a solution made up from 20 grams of trichloracetic acid, 100 ml. of ammonia sp. gr. 0·900 and 100 ml. of water.

(b) *Lead deposition* of about 0·25 gram of lead as PbO_2. Outer electrode anode. Add about 10 ml. of conc. nitric acid. Volume for glass frame electrodes 55–60 ml. For all-platinum electrodes, 70–80 ml. Heat to 95°, then switch on and adjust current to 5 amps. Keep temperature between 95° and 97°. Time for glass frame electrodes 15–20 minutes, for all-platinum electrodes 10 minutes. Dry in alcohol and ether as described. Use factor 0·865. For stripping, use dilute nitric acid to which hydrogen peroxide is added. Be careful to have anode perfectly free from grease by heating first to redness in a bunsen flame.

Preparation of the Auxiliary Saturated Calomel Electrode. 1 or 2 ml. of pure mercury are poured into the electrode vessel (Fig. 9 (VIII *)), then a layer of 1 or 2 mm. thickness of electrolytic calomel [1] made into a paste with saturated potassium chloride solution is introduced and the electrode vessel is almost filled with crystals of potassium chloride. The vessel may then be filled with saturated potassium chloride solution till it almost reaches the T bend in the connecting-tube and a rubber cork is then firmly inserted. The connecting liquid is then poured into the tap funnel and the connecting-tube filled by opening the tap and then closing. If preferred, the connecting liquid may be run also into the electrode vessel, provided that the latter has been charged with the potassium chloride crystals.

A Deposition under Controlled Potential of the Cathode. Depositions under controlled (or ' graded ') potential must be made in those cases where, should the cathode potential rise to too high a value, the constituent being determined may be deposited in a form unsuited to accurate analysis. In the case of bismuth, for example, if the potential be too high, the hydride is deposited and this, after loss of hydrogen, forms a metallic deposit which is spongy and but loosely adherent to the cathode.

The method of graded potential is also used in certain analyses in order that one constituent may be separated from, and determined in the presence of, another. In these separations, the rheostat R is used in shunt with the battery B, as better control of the potential is thereby obtained.

The following additions to the technique previously described above under (a) and (b) are then necessary. The auxiliary electrode is connected to the +ve, the cathode holder O to the —ve terminal, of the 50,000 ohms high resistance unipivot voltmeter, the connecting wires being taken along the hooks at the top of the stand so as to avoid fouling other apparatus. The shunt switch is closed and the tip of the auxiliary electrode is placed in the beaker outside the outer electrode about 1 cm. below its top. After

[1] Lipscomb and Hulett, *J. Amer. Chem. Soc.*, 1916, *38*, 21.

the motor has been started and the liquid taken to the proper temperature the current is adjusted to a suitable value and the high resistance voltmeter is read. The voltage is prevented from going above this initial value by adjustment of the current slider R. When the current has thus gone down to a value of, usually, about 0·2 amp. it is increased until the voltmeter registers an increase of 0·05 volt. At this reading the voltmeter is again kept constant by adjustment of the current until the latter has fallen to its previous lowest value. One or two more increases of 0·05 volt are made, the last voltage being maintained for 3 to 5 minutes.

Example. *Bismuth deposition* of about 0·25 gram of bismuth. Use as junction liquid in the auxiliary electrode a solution of 50 grams of sodium nitrate in 100 ml. of water. Volume of solution for glass frame electrodes, 50–60 ml. Add about 3 ml. of conc. nitric acid and 0·1 to 0·2 gram of hydrazine sulphate. Temperature about 80°. Current 1·6 amps. to minimum value. Auxiliary electrode 0·07 to 0·22 volt (increased towards end of determination by three steps each of 0·05 volt).

If the bismuth is to be separated from lead, replace the hydrazine sulphate by about 5 drops of 50 per cent hydrazine hydrate or by a solution of hydrazine nitrate.

The resistance of the electrolyte in the junction arm of the auxiliary electrode is usually less than 1,000 ohms for saturated potassium chloride ; for other electrolytes which are likely to be used it may vary between about 250 and 4,000 ohms. If the resistance of the voltmeter is 50,000 ohms the resistance in the junction arm would, according to the electrolyte used, cause the readings to be between $\frac{1}{2}$ per cent to about 10 per cent low.

For depositions under controlled potential the correction will usually be found negligible.[1] To determine the correction an amalgamated zinc rod may be clamped in the outer electrode clamp O of the stand and a beaker containing a zinc sulphate solution introduced from below. Into this the tip of the auxiliary electrode is also dipped. The auxiliary electrode is connected to the + ve terminal of the potentiometer box and the outer electrode clamp to the − ve terminal. The high resistance voltmeter is also connected to the potentiometer box. The following operations are then carried out. The switch A is turned to 'direct' and the voltmeter read. This reading, which we indicate by D, is the same as that which would have been obtained if the voltmeter had been connected to the two electrodes direct. To obtain the corrected reading, the push-pull battery switch is raised, the coarse adjustment knob having been turned to the extreme left, the fine adjustment knob to a central position.

The switch A is then turned to the potentiometer position, when a deflection will be obtained on the voltmeter. This is brought to zero by turning the coarse adjustment knob. The button on the voltmeter may then be depressed to short-circuit the series resistance, while the voltmeter is brought to zero with the greatest possible accuracy by means of the fine adjustment knob. The *cut-out button is then released* and the required P.D. is read on the voltmeter, after depressing the 'Read volts' button on the potentiometer. If we indicate this reading by P, the percentage correction

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[1] *Analyst,* 1934, *59,* 333.

for resistance of the connecting liquid to be applied to direct readings of the voltmeter is $100 \dfrac{P - D}{D}$.

Potentiometric Titrations. The electrolytic stand, in conjunction with the auxiliary electrode and the high resistance voltmeter, will be found very useful for the purpose of potentiometric titrations. In oxidation-reduction titrations, such as bichromate or quinhydrone titration, the inner electrode revolving in its glass tripod stand may be used as a combined indicator electrode and stirrer. The reversing switch RS is set to connect the slider to the inner electrode. For a titration in the direction alkali → acid or reduction → oxidation the terminal P of the stand is connected to the + ve, and the auxiliary electrode to the — ve terminal of the high resistance voltmeter. When the titration is in the opposite direction the connexions are reversed. If the pointer on the voltmeter should be at an inconvenient position at the beginning of a titration, it may be brought to zero position by the method of Roberts,[1] and for this purpose the terminal P is provided. About 2 volts are put on the battery terminals B of the electrolytic stand, the main and shunt switches are closed, the slider of the rheostat R started in about centre position and then moved up or down until the pointer of the voltmeter comes to zero or other convenient position. The burette, which should be fitted with a suitable tap extension, may either be clamped to a rod of the stand or, preferably, fitted to a stock bottle.

Example. *Bichromate titration.* Take 20 ml. of approximately N/10 FeSO$_4$, dilute to about 60 ml. and add 20 ml. of conc. hydrochloric acid. Use saturated calomel auxiliary electrode. Titrate to maximum change of voltmeter reading for 1·1 ml. titrant. If desired, plot a graph of voltmeter reading against millilitre titrant as abscissa. Point of inflexion on the graph gives millilitres of titrant at end-point.

Conductometric Analysis. The stand and voltmeter will be found useful in titration by the visual method. The conductivity vessel (Fig. 14 (VIII *)) is similar to that described by Britton and German.[2] It is provided with a fixed guide tube and stirrer. The former is held by the outer electrode clamp and the latter by the inner electrode clutch. The voltmeter is used as a galvanometer without series resistance, the special galvanometer terminal provided being employed. A Westinghouse G.B. rectifier is suitable for rectification.

Potentiometric *p*H Measurement. Sand's electrochemical apparatus is well adapted for measurements of *p*H potentiometrically. For this purpose the auxiliary electrode (Fig. 10 (VIII *)) is required, in conjunction with either a hydrogen or a quinhydrone electrode of suitable design. The auxiliary electrode is conveniently available on the universally adjustable clamp AE (Fig. 5 (VIII *)), and the hydrogen or other electrode may be supported in the outer electrode clamp O.

An auxiliary electrode frequently employed is the saturated calomel electrode, prepared as described. Leads are taken from the terminal on this and from the terminal on the hydrogen or the quinhydrone electrode, to the terminals marked X on the potentiometer box. In the calomel-hydrogen combination, the former is + ve. In the calomel-quinhydrone

[1] *J. Amer. Chem. Soc.*, 1919, *41*, 1358.   [2] *J. Chem. Soc.*, 1930, 1250.

combination the former is — ve. The voltmeter is then connected to the marked terminals on the box and the potentiometer system balanced and read in the manner described.

The potential of the saturated calomel electrode at 18° referred to the normal hydrogen electrode is 0·251 volt. If the E.M.F. of the calomel-hydrogen system, read as indicated above, is denoted by E^1 (volts), then the pH of the liquid under test is given by the formula

$$p\text{H} = 1{,}000 \left(\frac{E^1 - 0{\cdot}251}{58} \right)$$

With the quinhydrone electrode, which can be used in acid solutions only, i.e. solutions whose numerical pH value is less than 7, the formula becomes, at the same temperature (18°) and E indicating the E.M.F. of the quinhydrone electrode-calomel electrode system,

$$p\text{H} = 1{,}000 \left(\frac{0{\cdot}453 - E}{58} \right)$$

The possible accuracy of pH measurements carried out on this instrument is readily established. The voltmeter can be read by estimation to 1 millivolt and, since about 58 millivolts $= 1$ pH, the possible accuracy therefore becomes 0·02 pH.

An M/20 solution of potassium hydrogen phthalate forms a useful reference liquid for checking either the hydrogen or the quinhydrone electrode. It has a pH at 20° of 3·97.

It may be noted that the equipment comprised in Figs. 5 (VIII *) to 14 (VIII *) is capable of independent use and is convenient for potentiometric pH measurement.

SECTION 2: POLARIZATION PHENOMENA

General Considerations.—Let E represent the E.M.F. of the cell
Pt | H_2(1 atm. press.) | HCl(c) | Cl_2(1 atm.) | Pt where the cell reaction is

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 = HCl(c)$$
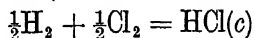
E is measured by a null method, by balancing the E.M.F. of the cell against an opposing external E.M.F. so that no current passes in either direction.

The reverse of this effect represents the electrolysis of hydrochloric acid and it is clear that in order to bring this about an E.M.F. e, greater than E, must be applied. E then acts as a counter or back E.M.F. and is equal to the *Decomposition Voltage*, which is the minimum voltage which must be applied to produce electrolysis.

During electrolysis, according to Ohm's law,

$$e - E = R.C$$

where C is the current and R is the resistance of the system. If e is only very slightly greater than E, the current density (current per unit of electrode area) will be very small and E will be very near the reversible E.M.F. of the cell. When e is considerably greater than E, the electrolysis which occurs causes physical and chemical changes in the system, which in turn cause E to vary from its reversible value. The cell and electrodes are then said to have undergone polarization.

Polarization is any change produced at an electrode by electrolysis which causes its potential to differ from its reversible or normal value.

The *Overvoltage* of an electrode is the difference between the potential of the electrode which has undergone polarization and its reversible electrode potential in a solution of the same concentration. Thus the overvoltage of the hydrogen electrode in the cell above would be equal to the E.M.F. of the reversible cell,

$$Pt \mid H_2(\text{depositing}) \mid HCl(c) \mid H_2(\text{reversible}) \mid Pt$$
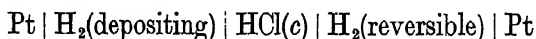
and could be measured by putting a reversible hydrogen electrode in the cell.

Concentration Polarization. Consider the cell

$$Cu \mid CuSO_4(c) \mid Cu$$

The electrodes are identical, so that the cell has no E.M.F. If however a current is passed electrolysis takes place, copper is deposited on the cathode so that the concentration of the copper sulphate here is reduced to c_1, while copper dissolves at the anode raising the concentration of the copper sulphate here to c_2: the cell has then been altered to the concentration cell

$$Cu \mid CuSO_4(c_1) \mid CuSO_4(c_2) \mid Cu$$
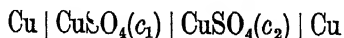
and this gives an E.M.F. opposing the applied E.M.F. This effect is called concentration polarization: it is increased by a high current density and

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can be decreased by stirring. In the absence of stirring diffusion will tend to reduce the polarization, but this process is a slow one.

Residual Current. If an electrolytic cell containing dilute sulphuric acid between platinum plates is connected in series with an ammeter and in parallel with a voltmeter, and gradually increasing voltages are applied, we get the following effects : for example, with an applied voltage of 0·5 volt, at the moment of application a large current passes which very rapidly drops almost to zero.

At the start the electrodes are similar; there is no back E.M.F., and a current can pass. The current produces hydrogen and oxygen on the plates to set up a back E.M.F. of 0·5 volt and so the current stops. The platinum plates are imperfectly converted into hydrogen and oxygen electrodes and are said to be polarized to half a volt. If the cell is now allowed to stand without the applied voltage, the polarization disappears and on repeating the experiment the large initial current will again be obtained. The oxygen and hydrogen on the plates are slightly soluble in water and so are able to diffuse away and escape into the air or recombine. This diffusion goes on while an external voltage is applied so that a small current will always flow, a current just large enough to replace the hydrogen and oxygen at the same rate as they are removed by diffusion. This small current is the residual current; it is very small with hydrogen and oxygen on account of the small solubility of these gases in water, but larger, for example, when hydrochloric acid is electrolysed because the chlorine is readily soluble in the water and diffuses over to the hydrogen on the cathode and combines with it to a considerable extent. For this reason Faraday's law will not hold exactly here.

If the voltage is raised from 0·5 to 1·0 volt there will again be a sudden flow of current which will quickly drop to the 'residual' value which, however, will be somewhat greater than before.

When the voltage is increased to 1·11 volts the electrodes become saturated with hydrogen and oxygen, the applied E.M.F. is equal to the E.M.F. of the reversible oxygen hydrogen cell, so that any increase in the applied E.M.F. should result in free electrolysis.

Here, however, comes in the complication of overvoltage referred to above and this depends on the nature of the metal of the electrodes ; with polished platinum the effect at the cathode is 0·09 volt and at the anode 0·59 volt so that to produce visible decomposition requires

$$1·11 + 0·09 + 0·59 = 1·79 \text{ volts}$$

The decomposition voltage alters with the concentration of the solution, thus, with normal hydrochloric acid it is 1·31 volts but with 0·03 N. HCl it has increased to 1·69 volts ; the result is that while electrolysis of concentrated solution yields hydrogen and chlorine, in dilute solution the products are hydrogen and oxygen because the decomposition potential of water has been reached.

Determination of the Decomposition Voltages of Hydrochloric, Hydrobromic and Hydriodic Acids in Normal Solutions. The apparatus required is shown in the diagram (Fig. 15 (VIII *)). The cell containing the normal hydrochloric acid has a stopper through which pass the

tubes carrying two electrodes ; of these the cathode is a platinum plate while the anode, at which the chlorine is liberated, is a platinum point.   A stream of hydrogen from a cylinder or a Kipp's apparatus is washed in N. HCl and then passes through the tube at the bottom of the cell over the platinum plate, so as to ensure that this is kept saturated with hydrogen at atmospheric pressure throughout the experiment, and then passes out through a small bubbler the purpose of which is to exclude air.
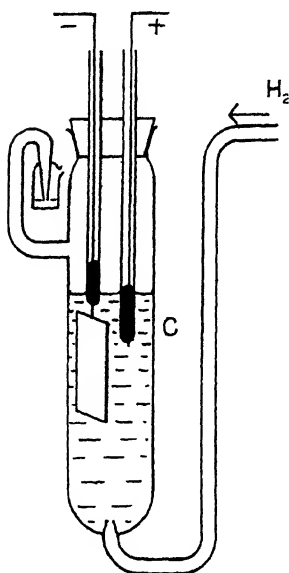
This cell is shown at C in Fig. 16 (VIII *), where R_2 is a sliding rheostat of about 100 ohms resistance through which a current from the single storage cell B is passed.   The cell C and the voltmeter V (0 to 2 volts) are connected to one end of this rheostat and both are also joined to the sliding contact thereon, the cell C by way of the galvano-meter G which has a shunt R_1 of about 20 ohms resistance.

G is a direct-reading galvanometer, having a resistance of about 100 ohms and a sensi-tivity of about 5 microamps. per scale division.

With this arrangement, provided that the resistance of the galvanometer with its shunt is small compared with the resistance of the cell C, the voltmeter will give readings which are sufficiently near to the E.M.F. applied across C.
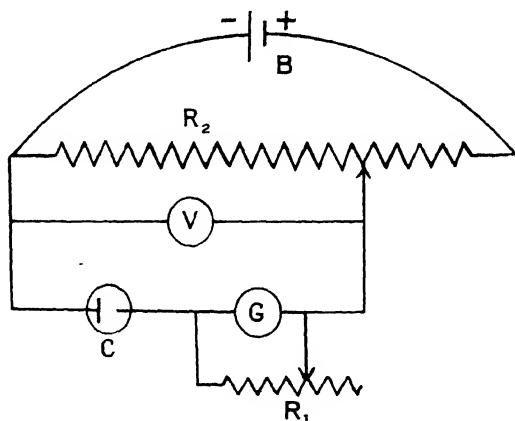

FIG. 15 (VIII *)

FIG. 16 (VIII *)

Move R_2 so that the voltmeter indicates 1·6 volts and then adjust R_1 so that the whole of the scale of the galvanometer is utilized.   Commence the experiment by adjusting R_2 to read 0·2 volt and after waiting 2 minutes

record the voltage and the current in C; increase the voltage to 0·4 and again record voltage and current. Proceed in this way by steps of 0·2 volt until an appreciable rise in the current strength is obtained, then go back to the last point and proceed from there by steps of 0·05 volt, waiting for 1 or 2 minutes after each setting before reading the current strength.

When the voltage has reached 1·6 take a set of readings with falling potentials and use the means of the two sets of values to plot a curve with current as ordinates and voltage as abscissae.

Try the effect on the residual current obtained with a low voltage, of stirring the liquid vigorously by increasing the current of hydrogen gas.

Next repeat the experiment with the addition of 0·2 gram of potassium bromide. The hydrochloric acid will set free some hydrobromic acid from the bromide and the effect of this will be observed; or alternatively the potassium bromide may be looked on as a depolarizer for the reason that the polarization of the anode is due to chlorine gas, but chlorine will immediately react with potassium bromide giving potassium chloride and free bromine, so that the chlorine layer is removed and its place taken by bromine, giving the same effect as if hydrobromic acid were being electrolysed.

Repeat the whole experiment with the addition of

1·0 gram of potassium bromide

then　　　　0·1 gram of potassium iodide

and　　　　0·5 gram of potassium iodide

Plot the results on squared paper and find the breaks in the curves corresponding to the decomposition potentials by extrapolating the straight line portions of the curves. Sharper breaks can be obtained by plotting the logs of the current against the voltage.

The Polarograph. When a pair of electrodes are immersed in a solution containing a number of reducible substances, for example, of metallic cations having different reduction potentials, and the cathode is polarized by an E.M.F. increasing gradually from zero upwards, no appreciable current will at first pass. As soon, however, as the lowest reduction potential is reached, a current proportional in strength to the concentration of the respective substance flows through the solution; when the next higher reduction potential is reached a sudden rise in the strength of the current occurs proportional to the concentration of the second substance of the series, and so on. The plotting of the current-E.M.F. curve thus amounts to a qualitative and quantitative analysis of the solution.

It was not till Hevrovsky [1] secured definite conditions of polarization by introducing the use of Kucera's mercury-dropping electrode and together with Shikata had added automatic recording of the current-E.M.F. curves by designing the polarograph that the method became a convenient one for analysis for scientific and industrial purposes. A suitable apparatus is made by E. Leybold's Nachfolger A.-G.

Arrangement of the Apparatus. *Electrolytic System.* The solution E (Fig. 17 (VIII *)) under test is contained in a small electrolytic vessel above a layer of mercury A which serves as anode. The cathode K also

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[1] See *Physikalische Methode in der chemischen Analyse*, W. Böttger, Akademische Verlags-Ges., Leipsig, Vol. 2.

consists of mercury. Small drops of mercury, fed from an adjustable storage vessel, are discharged slowly from a fine glass capillary into the electrolyte. The surface of this dropping cathode being constantly renewed, the conditions under which reduction takes place are simple and reproducible compared with those obtained at steady or rigid electrodes. The smallness of the surface area of the cathode compared with that of the anode prevents control of the recorded electrolysing current, that is, limitation of its strength, by the anode. The considerable overvoltage of hydrogen on mercury precludes trouble through generation of hydrogen.
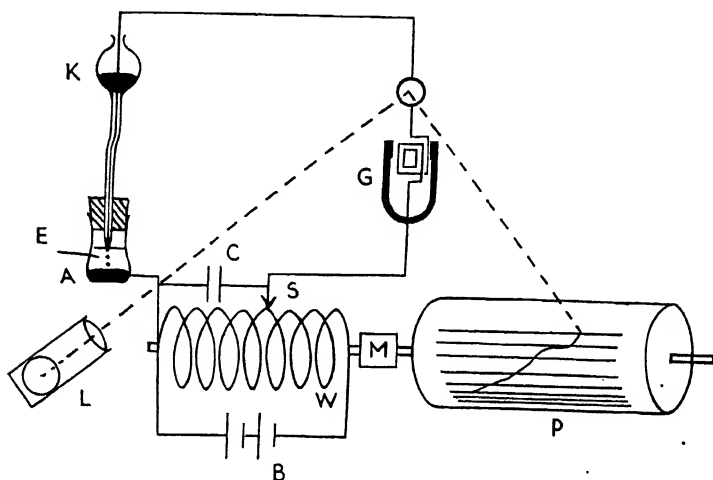
FIG. 17 (VIII *)

Electrical Equipment. To operate this electrolytic system in the manner outlined above it is necessary to apply an E.M.F. increasing slowly and uniformly from zero to the decomposition voltage of water (about 2·6 volts). This is done by means of a special precision potentiometer W, the wire resistance coil of which is connected to a storage battery B, of 2 or 4 volts. In the course of the analysis the small sliding contact S travels from one end of the wire resistance to the other, thereby adjusting a uniformly increasing voltage in the electrolytic circuit. The current flowing in the circuit, which, in its relation to the voltage applied, is the means of polarographic analysis, is read on a highly sensitive moving coil galvanometer G, the range of which is adjustable within wide limits.

Recording Device. The lamp L casts a fine pencil of light on to the mirror of the galvanometer, whence it is reflected on to a strip of sensitive paper P wound on a cylinder adapted to be rotated by the motor M. The stronger the current passing through the electrolyte, the greater will be the deflection of the mirror and the farther will the light pencil be displaced in the direction of the cylinder axis. This direction coincides with that of the current co-ordinate. The movement of the sliding contact S adjusting the voltage is positively coupled with the rotation of the recording cylinder and consequently also with the feed of the sensitive paper at right angles to the current co-ordinate; this direction, along the recording paper,

coincides with that of the voltage co-ordinate and the pencil of light traces
a current-voltage curve, a polarogram, as indicated above. A special
device traces line marks on the polarogram at equal intervals of voltage
by means of which the polarization voltage belonging to a definite rise of
current strength can be read.

Description of the Polarograph. All the parts of the instrument
are assembled in small compass in a metal case closed on all sides, par-
ticular care being taken to secure good electrical contacts. The electrolytic
system, the galvanometer lamp and the galvanometer itself are installed
separately. The polarograph (Fig. 18 (VIII *)) consists of a Kohlrausch's
potentiometer cylinder W rotated uniformly by the motor M and having
a wire of suitable quality and 16 ohms resistance wound on it in twenty
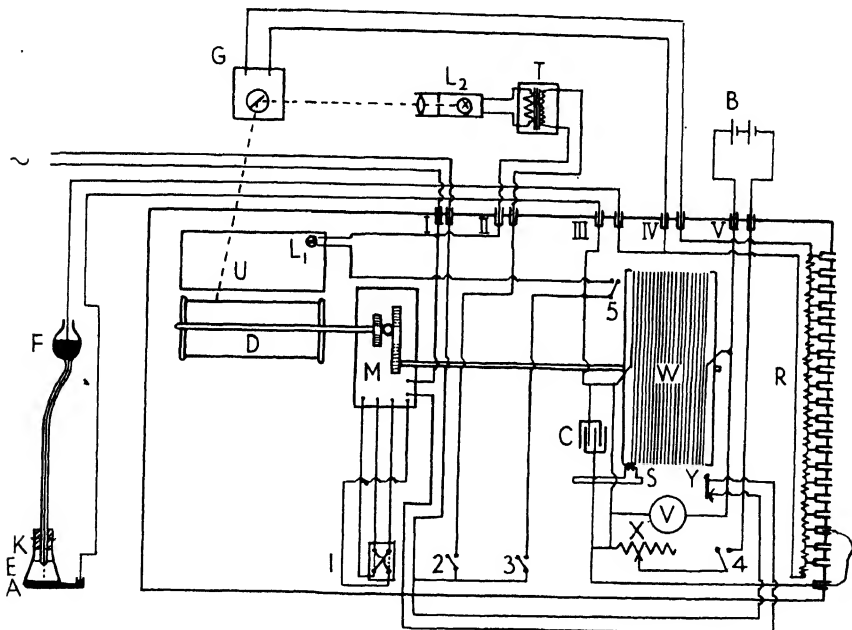
FIG. 18 (VIII *)

turns. A storage battery B, the voltage of which is read on the voltmeter V
and adjusted by means of the series resistance X, is connected to the poten-
tiometer. In consequence of the rotation of the cylinder W, the sliding
contact S travels slowly and with uniform velocity along the whole wire
and thereby adjusts a uniformly increasing voltage in the system cathode
K-solution E-anode A, which is steadied by the condenser C. The elec-
trolysing current passes through the galvanometer G provided with the
range switch in Ayrton connexion R by means of which any desired range
between 1/1 and 1/10,000 of the full sensitiveness can be adjusted. The
feeblest and the strongest current measurable by the instrument are as
1 is to 1,000,000, and this proportion agrees approximately with the range
of concentration within which a polarographic analysis is practicable. The
galvanometer, an instrument with damping resistance and long period of

oscillation, has a sensitiveness of $2\cdot3 \times 10^{-9}$ amps. and is illuminated by a lamp L_2. This lamp and the motor are connected to the mains through a transformer T. The pencil of light reflected from the mirror of the galvanometer passes through the box screen U, which cuts off the daylight and allows only the pencil of light emitted by the lamp L_2 to penetrate the recording cylinder D enclosed in a light-tight case. The recorder D consists of a rotatable interior cylinder on which the sensitive paper is wound and a fixed jacket cylinder in which is a narrow longitudinal slit provided with a cover. The potentiometer cylinder and the interior cylinder are driven by the same motor, the latter, however, at a twenty-times slower rate, so that the entire length of the potentiometer wire corresponds to a single revolution of the recording cylinder. At the end of each revolution, that is, twenty times during each record, the potentiometer cylinder operates the switch 5 controlling the lamp L_1. The light of the lamp falls for a moment on to the slit in the recorder jacket and thus marks the voltage lines on the polarogram.

The case of the polarograph is adapted to slide on two bars let into the base plate and can by this means be displaced laterally. A rotatable ring-shaped scale allows of adjusting the zero point of the curve to any desired part of the polarogram. By means of these two devices several curves can be traced on the same polarogram, and higher, and therefore more accurately measurable, current rises obtained. The voltage at which the tracing of the curve is to begin is adjusted by means of the rod projecting laterally from the case. On completing the automatic tracing of the curve, the apparatus is cut out automatically.

Example of an Analysis. The curves of Fig. 19 (VIII *) were obtained with a solution containing the chlorides of copper, lead, cadmium,
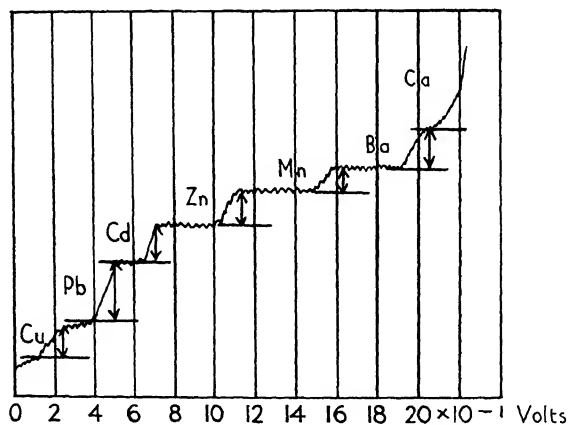

FIG. 19 (VIII *)

zinc, manganese, and barium in quantities of the same order of magnitude together with an excess of calcium chloride of about ten times that quantity. The calcium chloride serves as a so-called 'indifferent' electrolyte. As the steps in the curves are somewhat lower in solutions rich in ions than in solutions containing few ions, the practice has been adopted of working

in a solution rich in ions, in the present case calcium ions, the main part of which is reduced later than the ingredients to be estimated. By the presence of this indifferent electrolyte we are enabled to work throughout in solutions of about equal total ionic concentration and thus the steps in the current-voltage curves are in all cases strictly proportional to the concentration. The polarograph does not indicate the absolute quantity of the dissolved substance but the concentration of the solution. The indifferent electrolyte should therefore be added to the solution in a measuring flask and the latter filled up to the mark. The quantity taken for analysis is not measured.

As a storage battery of 4 volts was used, each line mark represents a voltage increase of 0·2 volt. It will be seen that each rise of current strength occurs at a definite voltage, the reduction potential.

Copper	at 0·1 volt	Zinc	at 1·05 volt
Lead	at 0·42 volt	Manganese	at 1·52 volt
Cadmium	at 0·62 volt	Barium	at 1·95 volt

	With the degree of sensitiveness used in tracing this polarogram, viz. 0·04, the heights of the individual steps are		With the full sensitiveness of the galvanometer they would therefore be :
Copper	.	10 mm.	. . 250 mm.
Lead .	.	20 mm.	. . 500 mm.
Cadmium	.	11 mm.	. . 275 mm.
Zinc .	.	9 mm.	. . 225 mm.
Manganese	.	7 mm.	. . 175 mm.
Barium	.	10 mm.	. . 250 mm.

Having calibrated the apparatus by means of a solution of known strength, we know that :

	Using the full sensitiveness of the galvanometer and provided that the solutions under test are of the same strength as the calibrating solution, a step of 1 mm. indicates		The analysed solution therefore contains
Copper	. . .	0·127 mg.	0·127 × 250 = 32 mg. of copper
Lead .	. . .	0·425 mg.	0·425 × 500 = 213 mg. of lead
Cadmium	. . .	0·225 mg.	0·225 × 275 = 62 mg. of cadmium
Zinc .	. . .	0·133 mg.	0·133 × 225 = 30 mg. of zinc
Manganese .	. .	0·109 mg.	0·109 × 175 = 19 mg. of manganese
Barium	. . .	0·270 mg.	0·270 × 250 = 68 mg. of barium

To increase the accuracy of the analysis the galvanometer must be plugged to a higher degree of sensitiveness. You then obtain parts of the same curve, merely enlarged in proportion to the increase in sensitiveness. The steps can thus be measured with greater accuracy. Polarimetric estimations do not, however, quite attain the limit of error of a good gravimetric microanalysis.

An example of a rapid analysis of an alloy of the nature of brass is shown in Fig. 20 (VIII *). A small cutting of the alloy was dissolved in a small measuring flask in 2 ml. of hot N. hydrochloric acid, neutralized with caustic soda to a very slight acidity and made up to 25 ml. The first polarigraphic curve was traced with a sensitiveness of 0·002 (curve a). The two smaller

steps were repeated in order to obtain more accurate measurements, the copper step with a sensitiveness of 0·005 (curve b) and the lead step with a sensitiveness of 0·01 (curve c). The indistinctness of the rises in current
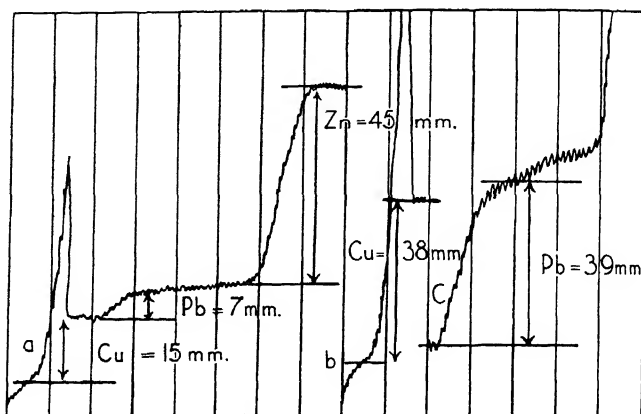

FIG. 20 (VIII *)

strength preceding the copper and zinc steps is due to dissolved atmospheric oxygen which in a more refined analysis would have to be removed by passing hy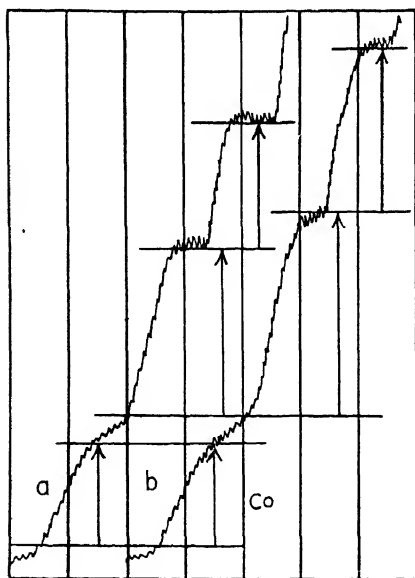drogen through the solution. A high peak of current strength overtops the copper current rise without, however, interfering with the measuring and evaluation of the curve. The time required for this analysis was 14 minutes.

FIG. 21 (VIII *)

Fig. 21 (VIII *) shows the determination of two solutions of insulin. Very dilute solutions of equal quantities of two preparations of insulin, a and b, were made in physiological sodium chloride solution and 2 ml. of each added to equal quantities of an indifferent solution of cobalt chloride, ammonium chloride and ammonium hydroxide in suitable strength. The two polarograms show equally high cobalt steps. On the other hand, the two double steps of insulin differ in height from each other by 0·2.

The method has very wide applications in physical chemistry, investigations in pharmacology, medicine, and biology and for works tests in industrial laboratories.

SECTION 3 : REDUCTION AND OXIDATION

A.   REDUCTION [1]

The reduction of organic substances, by electro-chemical methods, has not, as yet, wholly received the attention which it deserves. It possesses many advantages over the ordinary methods of reduction (addition of a chemical reducing agent), chief amongst which are (a) that unlike the latter no oxidized substance is introduced into the solution and (b) that the stage of reduction can be varied within fairly wide limits by suitable choice of cathode material and cathode potential.

If hydrogen ions are being discharged at a cathode in an electrolyte containing a reducible substance, reduction of the latter may occur instead of evolution of hydrogen. Such reductions may be divided into two classes :

(1) Those in which there is an alteration of a charge on an ion,

$$\text{e.g. } Fe^{\cdots} \longrightarrow Fe^{\cdot\cdot} + \oplus$$
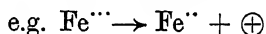
(2) Those in which the hydrogen content of the substance is increased or its oxygen content decreased,

$$\text{e.g. } C_6H_5NO_2 + 6H^{\cdot} \longrightarrow C_6H_5NH_2 + 2H_2O + 6\oplus$$
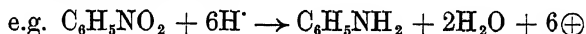
It is proposed to deal only with examples of the latter class here. Usually in electrolysis of acid or alkaline solutions between permanent electrodes hydrogen is evolved at the cathode and oxygen at the anode. To bring about hydrogen evolution, even when working at small current densities, some polarization is generally necessary. The amount is dependent on many factors but principally on the nature of the cathode material and on the current density employed. The polarization necessary to cause evolution of hydrogen at a cathode, under given conditions, is called the over-voltage of the cathode for hydrogen. The hydrogen over-voltage of a given material at a given current density, temperature, &c., is therefore the difference between the cathode potential necessary to cause evolution of hydrogen at that electrode and the equilibrium potential of hydrogen in the same electrolyte. It is because of this over-voltage phenomenon that the process of electrolytic reduction is of practical importance. It represents not merely an increased energy expenditure in the separation of hydrogen, but on account of the change in electrode potential that it causes it may alter the nature of the electrode process. The type of cathode, therefore, can affect electrolytic reduction by increasing the polarization required for the discharge of H$^{\cdot}$ ions. If the cathode used allows reversible H$^{\cdot}$ ion discharge, only evolution of hydrogen will take place. If, however, its hydrogen over-voltage be at all considerable reduction will occur.

[1] This section was revised by Dr. P. J. Drumm for the 2nd ed.

For substances which are reduced only with difficulty a cathode of lead, mercury or zinc is required as the hydrogen over-voltage at these electrodes is greatest.

Whilst the products of electrolytic reduction are influenced by the material of the cathode they are also dependent on the nature of the electrolyte, the current density employed and, to a lesser extent, on the temperature at which reduction is effected. In addition the cathodic material may exert a catalytic effect. Reaction between the depolarizer and hydrogen is catalysed at different rates by different cathodes, with the result that the same process may take place with a much less negative cathode potential at some cathodes than at others. Thus nitro-benzene, in acid solutions, is more readily reduced to aniline at a zinc cathode than at a platinum cathode. The physical condition of a cathode may also be a factor of some importance. Reduction of nitrates to ammonia proceeds readily at a smooth copper electrode ; at a spongy copper electrode reduction stops at the nitrite stage.

The following table shows the effect of variation of some of these factors on the products of reduction of nitrobenzene and acetone :

Substance	Cathode liquid	Anode liquid	Electrodes	Current density (amps. per sq. cm.)	Product
Nitro-benzene	50% Sulphuric acid	40% Sulphuric acid	Carbon cathode Lead anode	0·06	p-amino-phenol
,,	3% Sodium hydroxide	Sodium sulphate solution sulphuric acid	Nickel cathode Lead anode	0·05–0·07	Azoxyben-zene
,,	Ethyl alcohol + Sodium acetate	Sodium carbonate solution	Nickel cathode Platinum anode	0·06–0·08	Azobenzene
,,	,,	·,,	,,	0·06 at first, then 0·02	Hydrazo-benzene
Acetone	30–60% sulphuric acid	20% sulphuric acid	Mercury cathode Lead anode	0·04	Isopropyl alcohol
,,	,,	,,	Lead cathode Lead anode	,,	Isopropyl alcohol + Pinacone

Whilst the choice of cathode, electrolyte, and current density are matters for preliminary trial, it may be stated that for substances which are reduced with difficulty, e.g. reduction of CO group of ketones to CHOH and CH_2, or reduction of CO group of amides or esters to CH_2, the use of lead or mercury cathodes is indicated. In this connection it is important that the electrolytes should not contain even traces of salts of metals which have a low hydrogen over-voltage and which may be deposited

on the cathode. When such salts are present no reduction may take place, only hydrogen being evolved.

The addition of certain substances to the electrolyte often has a beneficial effect on the yield of the reaction product. Thus the reduction of quinone to hydroquinone in acid solution is facilitated by the presence of titanium chloride. In the absence of the latter, reduction stops at the quinhydrone stage. Again Loeb found that the reduction of nitrobenzene to aniline was facilitated by addition of copper powder, whilst Kindler [1] has shown that greatly increased yields of tertiary amines are obtained in the electrolytic reduction of N-dialkylamides in acid solution by the addition of arsenious or antimony oxides.

The temperature at which reduction is carried out is sometimes of much importance. A rise of temperature acts favourably by increasing the velocity of diffusion of the depolarizer. But it also lowers to a small extent the hydrogen over-voltage, thus facilitating hydrogen discharge. The choice of a high or low temperature will therefore depend on which of these two effects predominates. Law has found that by reduction of benzaldehyde in acid solution at low temperatures a good yield of benzyl alcohol is obtained, whereas at high temperatures the hydrobenzoins are principally formed, thus showing that, in this case, the least amount of reduction takes place at high temperatures. On the other hand, reduction of caffeine and allied substances is facilitated by an increase of temperature.

It is sometimes necessary, especially where side reactions occur, to reduce the time taken for reduction. This is usually effected by an increase of current density although it must be remembered that this tends to raise the temperature. From the experiments of Tafel it would appear that the use of a superficially oxidized cathode which, at the commencement, is covered with a film of spongy lead has a marked effect in accelerating the rate of reduction with lead electrodes. He further states that the time taken for the reduction of large or small quantities is approximately the same, provided the initial concentration of the depolarizer, the current concentration per litre of cathode liquid and the proportions (usually 1 : 1 or 1 : 2) between the area of the cathode and the volume of the cathode liquid are maintained the same.

In reductions where sulphuric acid is used as liquid, Tafel has found that in general it is best to use dilute acid, but a limit is sometimes set by the fact that not all substances are soluble in dilute acid. An acid containing up to 95 per cent sulphuric acid may also be employed, but here there is the possibility that the acid itself may undergo reduction with deposition of sulphur. As regards the anode compartment, it is not advisable to use an acid containing more than 70 per cent sulphuric acid on account of the great increase in anodic resistance with stronger acids.

Finally, it is of the utmost importance, especially in large-scale reductions, to provide efficient stirring of the cathodic solution as reduction tends to take place in the immediate vicinity of the cathode surface.

As the electrodes form the most important part of the cell, care should be taken in their selection. There is a considerable choice of metals as cathodes, since a large number may be considered as unattackable in dilute

[1] *Ber.*, 1923, *56*, 2063.

acid, alkaline or neutral solutions, for even in such solutions as are capable of attacking these metals, the cathode is protected during the passage of the current. In strongly acid solutions, copper, and often nickel and lead, are suitable, whilst in strongly alkaline solutions, copper, nickel, and iron are satisfactory. As materials for unattackable anodes consideration is confined to platinum, carbon, nickel, iron and lead. Carbon may only be used when no oxygen is evolved at the anode. Nickel anodes are permanent in alkalies and in alkaline carbonates in the absence of ammonia. In the case of iron there is the possibility that ferrites and ferrates may be formed in alkaline solution, but this metal may be employed in sulphuric acid solutions of specific gravity higher than 1·7 and in nitric acid solutions of specific gravity higher than 1·3.

An electrolytic reduction apparatus is of simple construction. The following particulars for a cell with lead electrodes may be considered as typical. The cathode and anode compartments are separated by a diaphragm, usually a porous pot, which allows the passage of the current but prevents access of the depolarizer to the anode. In large-scale operations where efficient temperature control of the cathode liquid is desirable, the cathode is made larger than the anode. The cathode is a cylindrical lead beaker with a glass plate resting on the bottom. Inside the cylinder stands a porous pot (anode compartment) in the centre of which is the anode. This may take the form of a roll of lead foil or, if cooling is required, of a hollow lead cylinder fitted with a double-holed rubber cork to allow circulation of a stream of cold water. The solution of the depolarizer in the appropriate electrolyte is introduced into the cathode compartment and the anode liquid into the porous pot. Care is taken to maintain the liquids in both compartments at the same level throughout the experiment. An ammeter, rheostat, and storage cells (sufficient to provide the necessary voltage) in series with the electrolytic cell complete the arrangement. Reduction is usually finished when hydrogen is freely evolved in the form of bubbles at the cathode surface. It
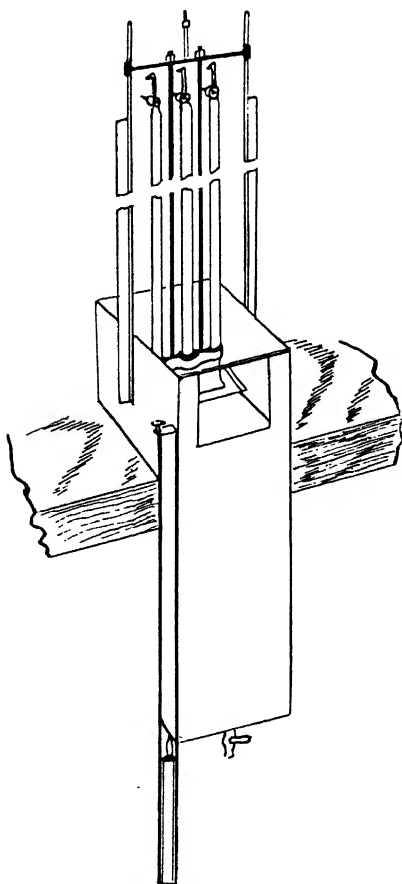
FIG. 22 (VIII *)

is essential to provide efficient stirring of the cathode liquid, but this may be dispensed with in small-scale experiments. (Fig. 22 (VIII *)).

Tafel recommends attention to the following points. The cathode, which should consist of pure lead, is first polished with wet sand. It is then electrolytically oxidized for half an hour in dilute sulphuric acid solution, using a current density of 0·02 amps. per square centimetre of surface. It is afterwards washed with cold water, and placed in boiling water for a few minutes. Finally it is washed with boiling alcohol and then quickly dried in a current of air.

With the exception of the polishing with sand this treatment should be repeated each time before use. The anode is initially treated in the same way, but for subsequent operations it is sufficient to wash with warm water and dry quickly.

The porous pot may contain traces of foreign metals. To remove these it is digested with dilute caustic soda solution for some time ; then completely immersed in a 5 per cent hydrochloric acid solution and acid drawn through the walls by suction for a considerable time. The acid is finally replaced by distilled water and the above operation continued. The pot is lastly dried at 100°. Porous pots should be preserved by immersion in distilled water which should be replaced from time to time.

Reduction of Nitrobenzene to Azobenzene. A porous pot of 6 cm. diameter is placed in the centre of a tall litre beaker. The pot contains as anode a roll of lead foil and as anode liquid a hot saturated solution of sodium carbonate. Around the outside of the pot is a closely fitting cylinder of nickel gauze. The cathode solution consists of 18 grams of nitrobenzene dissolved in 200 ml. of 70 per cent alcohol, containing 5 grams of sodium acetate (to increase the conductivity). Both solutions are previously heated to 70°. The heat developed during the passage of the current is then sufficient to maintain the required temperature. The upper part of the beaker is surrounded by several windings of rubber tubing through which circulate a stream of cold water. Thus any alcohol which vaporizes is condensed on the cold part of the beaker and is returned to the solution. The anode, before use, should be freed from adhering lead dioxide, so that the bare metal surface is exposed. A current strength of 6–7 amps. is employed. Reduction is generally complete in 130–160 minutes. As soon as a vigorous evolution of hydrogen commences the current is reduced to 1–2 amps. and the operation continued until hydrogen is again evolved.

The hot cathode liquid now contains, besides azobenzene, a small amount of azoxybenzene and some hydrazobenzene. Air is drawn through the liquid to oxidize the hydrazobenzene to the azo compound. The greater portion of the azobenzene crystallizes out on cooling and is nearly chemically pure. The yield is over 90 per cent. The current efficiency is about 90 per cent.

Calculation of Current Efficiency. From the equation :

$$2C_6H_5NO_2 + 8H^{\cdot} = C_6H_5NNC_6H_5 + 4H_2O$$
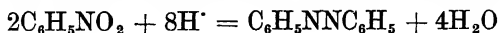
$8 \times 96,494 = 7 \cdot 72 \times 10^5$ coulombs (214·4 amp.-hours) are required for the reduction of 246 grams of nitrobenzene, therefore, $5 \cdot 64 \times 10^4$ coulombs (15·65 amp.-hours) are required for the reduction of 18 grams of nitro-

benzene. Hence if a current strength of 7 amps. for 144 minutes (16·8 amp.-hours) was employed, the current efficiency is

$$\frac{15\cdot65 \times 100}{16\cdot80} = 93\cdot2 \text{ per cent.}$$

Reduction of Benzophenone to Benzhydrol. Electrolytic reduction of purely aromatic ketones in moderately acid solution at lead electrodes yields principally pinacones together with small amounts of secondary alcohols. In weak alkaline solution, however, the latter may be obtained in good yield. A porous pot containing a cold saturated solution of sodium carbonate as anode liquid is surrounded by a perforated lead cylinder which acts as cathode. The anode is a lead plate. The cathode liquid consists of 30 grams of benzophenone dissolved in 500 ml. alcohol (96 per cent), 100 ml. of water and 6 grams of crystallized sodium acetate. A current density of 0·004 to 0·008 amps. per square centimetre is employed. Reduction is carried out at the boiling-point of the alcoholic solution. Evolution of hydrogen becomes pronounced only towards the end of the reduction. Instead of the theoretical quantity (8·9) about 10 amp.-hours are required. The time taken for reduction is 5 hours. The cathode liquid is neutralized with sulphuric acid, alcohol removed and the residual oil washed with water. It slowly solidifies. The solid is collected, dried and crystallized from petroleum ether. The yield of benzhydrol is 90 per cent. The current efficiency is about 80–90 per cent.
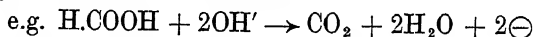
B. OXIDATION

Electrolytic oxidation processes may be divided into two classes :

(a) Those involving a decrease in the number of negative charges or an increase in the number of positive charges on an ion,

e.g. $Fe^{\cdot\cdot} + \oplus \rightarrow Fe^{\cdot\cdot\cdot}$
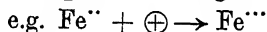
(b) Those involving an increase in the oxygen content or a decrease in the hydrogen content of a substance

e.g. $H.COOH + 2OH' \rightarrow CO_2 + 2H_2O + 2\ominus$

Only the latter class will be considered here.

Organic compounds may be oxidized by the oxygen evolved at the anode of an electrolytic cell. The oxidizing power of an anode is related to the potential difference between the electrode and the solution in the same way as is the reducing power of a cathode. There is also an over-voltage for oxygen which may attain considerable values. However, the order of decreasing oxygen over-voltages is different from that for hydrogen over-voltages. The oxygen over-voltage at platinum or gold electrodes is greatest, that for iron and nickel being much smaller. The number of metals suitable for use as anodes is considerably less than the number which can be used as cathodes. Platinum, lead and carbon are the principal electrodes in use in acid solutions, whilst in addition to the foregoing nickel and iron may be employed in alkaline solution.

Changes of current density, temperature and concentration act as in cathodic reduction. A high concentration of depolarizer keeps down the anode potential, which again is increased by increase of current density.

The nature of the anode material is of much importance, partly because

of its oxygen over-voltage and partly on account of its catalytic effect. The over-voltage at a smooth platinum anode being higher than at nickel or iron electrodes, it follows that for a substance which is oxidized only with difficulty at a high anode potential, a smooth platinum anode and a high current density are required. If, however, the current efficiency is less than 100 per cent (oxygen evolution) and the materials present may be further oxidized, the use of an iron or nickel anode is indicated.

The catalytic action of the anode material may be very considerable. Thus when iodic acid is oxidized at a smooth platinum electrode the yield is only 1 per cent ; with lead peroxide as electrode, the yield is theoretical.

The addition of certain substances called ' oxygen carriers ' to the anolyte has sometimes a marked beneficial effect on the course of the reaction. Thus cerous sulphate is anodically oxidized to ceric sulphate which is a vigorous oxidizing agent. The latter then reacts with the depolarizer, regenerating cerous sulphate. A further example is the use of manganous sulphate in the oxidation of anthracene to anthraquinone in acid solution at a lead anode.

Electrolytic oxidation methods, however, have not been much used mainly on account of the difficulty of arresting the reaction at the desired point. The reversible potentials at which a number of oxidations begin are usually much nearer to the potential required for free oxygen evolution than are the corresponding potentials in electrolytic reductions to that for hydrogen evolution. Hence the potential for oxygen evolution is attained at relatively low current densities. The yield of oxidized substance then falls below the theoretical. Once this has occurred the gradually increasing oxygen over-voltage is accompanied by an increase in anodic polarization. As a result the oxidizing potential increases to such an extent that oxidation of the substance proceeds much too vigorously, with consequent diminution in the yield.

Preparation of Iodoform. Thirty grams of anhydrous sodium carbonate and 30 grams of potassium iodide are dissolved in 300 ml. of water and 75 ml. of absolute alcohol are added. The anode is a sheet of platinum and the cathode a spiral of platinum wire. The liquid is maintained at 60° and a current of 2 amps. per square decimetre of anode surface is used. During the electrolysis a current of carbon dioxide is passed through the liquid. In this way approximate neutralization of the free alkali formed at the cathode and efficient stirring are effected (Fig. 23 (VIII *)).
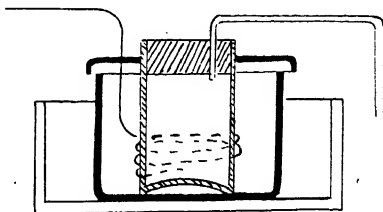

FIG. 23 (VIII *)

It is advantageous to use a rotating anode. Should the solution become brown during electrolysis owing to the liberation of iodine, too much carbon dioxide is being passed ; the supply should therefore be diminished or cut off. After passage of current for 3 hours the electrolysis is stopped. The reaction mixture is allowed to stand overnight and the iodoform which separates is filtered off. The current efficiency is about 80 per cent.

SECTION 4: ELECTRO-OSMOSIS WATER PURIFICATION

Ordinary water supplies usually contain from 100 to 600 parts per million of dissolved solids, usually present in the form of inorganic salts. In order to separate water from this mixture sufficiently pure for most uses in the physical chemical laboratory, it has been the practice to distil the water, converting the whole bulk of the water into steam and then condensing this. Owing to the high value of the latent heat of vaporization this is an expensive process and recently attempts have been made to cheapen the process by trying to remove the components present in small quantity and so leave the pure water as a residue.

When the dissolved substances are electrolytes, as is generally the case, they can be removed by electrolysis: for example, if the dissolved substance is calcium sulphate and two electrodes are put into the solution the positively charged calcium ions will travel towards the cathode, where they will form calcium hydroxide, and the negatively charged sulphate ions will move to the anode, there to form sulphuric acid: if the cell is divided into three parts by means of porous diaphragms and the electrodes are in the outer compartments, the ions will eventually all be removed from the central compartment, leaving there pure water.

Cells for this purpose have been described by Behrman [1] and Billiter, [2] and an apparatus has been put on the market by Siemens-Elektro-Osmose Gesellschaft m.b.H., Berlin, Siemensstadt.

It is desirable to maintain a continuous flow through the central compartment, but this would not be possible with a single cell, so a series or cascade of from ten to twenty cells is used and the water flows through the middle compartment of each cell in turn.

The apparatus may be run directly off the 220-volt D.C. mains. Since the concentration of dissolved substances decreases as the water passes through the cells, the resistance of the last cell is higher than that of the earlier ones so that, for example, in a cascade of ten cells, the first four cells may be connected in series, giving 55 volts across each cell, the next three cells are also in series, and again the next two (giving 110 volts across each of these cells), and finally the whole voltage is applied across the last cell. The rate of flow of the water is of course adjusted to the capacity of the set and the liquid in the electrode compartments also has to be flushed out: in a twenty-unit set the first sixteen units are flushed with untreated water and the last four with some of the purified water, the amount of the latter used for this purpose amounting to about 8 per cent of that produced. The liquid in the cathode compartments becomes alkaline, so that the water there becomes partially softened, and if this water is fed into the central

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[1] *Ind. and Eng. Chem.*, 1927, *19*, 1229.
[2] *J. Trans. Electro-Chem. Soc.*, 1931, *60*, 217.

compartments instead of untreated water an increase of about 30 per cent in the efficiency of the apparatus may be secured, and this is particularly desirable when the original water is rich in dissolved salts.

The current efficiency of the apparatus is about 20 per cent and is independent of the temperature : it is curious that the efficiency is less with water having a large salt content.

The purified water contains from 6 to 9 parts of dissolved solids per million, has a specific conductivity about 2×10^{-6} reciprocal ohms and a pH value between 6·8 and 7·2 : it is also sterilized by passage through the cells.

The Siemens cells are rectangular in plan with two parallel diaphragms ; these may be made of such materials as cloth, either plain or impregnated, asbestos cloth, chrome leather, or may consist of ceramic plates. The electrodes also consist of parallel plates, the cathodes being of zinc and the anodes of graphite, gas carbon, or magnetite.

The Billiter cells are cylindrical and have two concentric diaphragms which may have an area as large as 10 to 15 square feet : they are operable on from 7 to 200 volts D.C.

The relative cost of preparing distilled water by gas heating, coal heating, or the Siemens process can be calculated to suit local ruling prices from the following figures :

	100 litres of water cost
	s. d.
Using gas at 4s. 9d. per 1,000 cubic feet	3 10½
Using coal at £1 15s. 10d. per ton	9
Using electricity at 1¼d. per kilowatt-hour	3¾

The current consumption varies with the composition of the untreated water from 1·5 to 3·5 kilowatt-hours for 100 litres of water, and this may be reduced by 30 per cent by using the cathode water as explained above.

An idea of the size of the apparatus and the output obtained is given by the following :

Type	Dimensions in cm.	Weight	Hourly output in litres if total solids in parts per million is		
			100 to 200	200 to 350	350 to 600
IV	85 × 35 × 40	65 Kg.	4 to 6	3·5 to 5	2·5 to 3·5
I	220 × 170 × 180	3,300 Kg.	220 to 300	150 to 250	120 to 150

An automatic device may be included which shuts off the water supply if the current ceases, and since the apparatus requires no attention it can be run continuously for the 24 hours. Other advantages are the small space occupied, no safety regulations are required, no cooling water is necessary and no time or energy is wasted in starting up or stopping.

By using a more rapid rate of flow than is used for complete purification, partial softening to any degree may be produced. See also Barton and Jehans [1] and Barton.[2]

[1] *Ind. and Eng. Chem.*, 1930, 22, 1020.
[2] *J. Amer. Waterworks Ass.*, 1930, 22, 1115.

CHAPTER IX *

INDICATORS

SECTION 1 : GENERAL INDICATORS

ACIDIMETRY and **Alkalimetry.** Colour indicators used for the determination of the transition from acidity to alkalinity or the reverse are generally organic substances which act either as weak acids or bases and in which the undissociated form differs in colour from the ionic form or alternatively in which the ionogen form has a different colour (and constitution) from the pseudo or normal form.

Taking as an example a weak acid dissolved in water and dissociated according to the equation
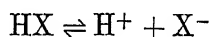
$$HX \rightleftharpoons H^+ + X^-$$

HX has the colour of the undissociated acid and X^- that of the ion which will be seen in the alkaline solution. The proportions of the two colours are obtained by applying the mass action law

$$\frac{[H^+][X^-]}{[HX]} = K_{HX}$$

or

$$\frac{[X^-]}{[HX]} = \frac{K_{HX}}{[H^+]}$$

where K_{HX} is the dissociation constant of the indicator.

On adding acid or base the colour ratio must change gradually with the alteration in the hydrogen-ion concentration. In practice there is a limit to which one can detect the change in one colour in the presence of excess of the other, and so a limiting range over which a colour change can be observed : this is the transition range for that particular indicator. Examples are given in the following table :

Substance	Transition range in pH	Colour change	
Picric acid .	0·0– 1·3	Colourless	to yellow
Methyl violet .	0·1– 1·5	Yellow	blue
m-Cresol purple	0·5– 2·5	Red	yellow
Thymol blue .	1·2– 2·8	Red	yellow
Methyl orange	3·1– 4·4	Red	orange-yellow
Bromphenol blue	3·0– 4·6	Yellow	blue
Congo red .	3·0– 5·2	Blue-violet	red-orange
Methyl red .	4·2– 6·3	Red	yellow
Lacmoid . .	4·0– 6·4	Orange-red	violet
Azolitmin .	5·0– 8·0	Red	blue
Bromcresol purple	5·2– 6·8	Yellow	violet
Bromthymol blue	6·0– 7·6	Yellow	blue

Substance					Transition range in pH	Colou	
Phenol red	.	.	.	.	6·8– 8·4	Yellow	to red
Cresol red	.	.	.	.	7·2– 8·8	Yellow	,, purple
Thymol blue	.	.	.	.	8·0– 9·6	Yellow	,, blue
Phenolphthalein	.	.	.	.	8·3–10·0	Colourless	,, violet-red
Thymolphthalein	.	.	.	.	9·3–10·5	Colourless	,, blue
Alizarin blue S	.	.	.	.	11·0–13·0	Green	,, violet

The transition range is affected by conditions such as temperature, presence of neutral salts, proteins, &c. A rise of temperature displaces the colour of acid-sensitive indicators towards the acid side and of basic sensitive ones towards the basic side. Neutral salts tend to displace the acid-sensitive type towards the basic side.

Choice of Indicators. This depends on the strengths of the acids and bases being used. With strong acids and bases in normal solution any indicator which changes between pH 3 and 11 may be used, with N/10 solutions the pH range must be between 4 and 10, and so on.

When a weak acid is titrated with a strong base the dissociation constant of the acid and its concentration are the important factors. Kolthoff [1] gives a table showing the pH at the equivalent point with acids of various dissociation constants and in N, N/10, and N/100 concentration when titrated with strong alkali : by giving also the pH 0·2 per cent before and 0·2 per cent after the equivalence point he indicates the pH jump at the end-point. He gives a similar table for the titration of weak bases with a strong acid. [2] With weak acids titrated with weak bases the end-point is too indefinite to make the colour method useful.

Indicators Making Use of Solubility Differences. 1. When the titrating solution is added to a mixture of two substances with both of which it produces a precipitate, the substance yielding the less insoluble precipitate may be used as an indicator for the substance giving the less soluble precipitate provided that the differences of the solubility products of the two precipitates is suitable and that suitable colour differences exist between the two precipitates. An example is the well-known case of the use of potassium chromate as an internal indicator in the titration of chlorides with silver nitrate. Here the solubility product of the silver chloride is much less than that of chromate, and while the former is white the latter is brick red.

Suppose that the silver and chloride solutions are normal and that the solubility products of silver chloride and the silver salt of the indicator are 10^{-10} and 10^{-6} respectively, and the concentration of the indicator is 10^{-2} normal.

At the end-point of the titration of the chloride the silver concentration will be 10^{-5}, at any point before this it will be less than 10^{-5} because the chloride concentration will be greater than 10^{-5}, hence the product of silver and indicator concentrations at the end-point will be 10^{-7}, i.e. less than the solubility product of the silver salt of the indicator.

A drop of N. Silver nitrate added to 50 ml. of the solution makes the silver concentration 10^{-3} and the product becomes 10^{-5}, which is greater

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[1] *Volumetric analysis*, J. Wiley and Sons.
[2] These tables are reproduced in *Thorpe's Dictionary Supplement*, 1935, **2**, 620.

than the solubility product of the silver-indicator salt, so this is then precipitated. In the case of potassium chromate no permanent precipitate of silver chromate will be obtained till all the silver chloride is precipitated, then the addition of a drop of normal silver nitrate exceeds the solubility product of silver chromate and this is precipitated with the formation of the brick-red colour. This type of indicator is obviously unsuited for very dilute solutions.

2. A somewhat different type of indicator is illustrated by the use of a suspension of the very insoluble silver iodide as indicator in the titration of nickel salts with potassium cyanide : here the reactions depend on complex formation.

The first reaction is that represented by the equation

$$NiCl_2.6NH_3 + 4KCN = K_2(NiC_4N_4) + 6NH_3 + 2KCl$$
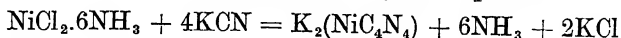
and when this is complete an excess of KCN reacts with the suspension of silver iodide according to the equation

$$AgI + 2KCN = K(AgC_2N_2) + KI$$
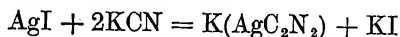
so that the turbidity of the solution disappears, thus marking the end-point.

Oxidation-reduction indicators are considered in the next section. Adsorption indicators are considered in Chap. V *, Section 2.

SECTION 2: OXIDATION-REDUCTION INDICATORS

The term oxidation is used to cover the three cases of addition of oxygen, removal of hydrogen, or the loss of electrons such as occurs in the oxidation of ferrous to ferric ions.

For convenience in the theoretical treatment it is convenient to regard the first two cases as being electronic : thus the oxidation of hydroquinone to quinone may be represented

$$H_2Q - 2H^+ - 2e \rightleftharpoons Q$$
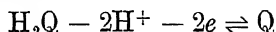
In a similar way reduction may be represented in all cases as being due to gain of electrons.

If we write as a general equation

$$\text{Oxidized form} + n.e \rightleftharpoons \text{Reduced Form}$$

where n represents the number of electrons and the system is reversible in the thermodynamic sense, the potential, E, of an unattackable electrode compared with that of the normal hydrogen electrode will be given by the equation

$$E = E_0 + \frac{RT}{nF}.\log_e\frac{[\text{ox. state}]}{[\text{red. state}]}$$

the terms R, T, n, and F having the same significance as on p. 457, and E_0 being a constant for the given system, called the standard oxidation-reduction potential.

In a system such as ferrous-ferric iron, for example, the value of E_0 would be the potential acquired by a platinum electrode against the normal hydrogen electrode in a solution containing equal concentrations of ferrous and ferric ions.

In certain cases the equation is not so straightforward ; take for example the oxidation by acid permanganate represented by the equation

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{++} + 4H_2O$$
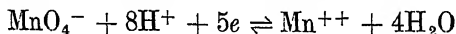
The electrode potential is then

$$E = E_0 + \frac{RT}{nF}.\log_e\frac{[MnO_4^-][H^+]^8}{[Mn^{++}]}$$

we may write this

$$E = E_0 + \frac{RT}{5F}.\log_e\frac{[MnO_4^{--}]}{[Mn^{++}]} + \frac{8RT}{5F}.\log_e[H^+] :$$

for a given concentration of hydrogen ions

$$E_0' = E_0 + \frac{8RT}{5F}.\log_e[H^+]$$

and

$$E = E_0' + \frac{RT}{5F}.\log_e\frac{[MnO_4^-]}{[Mn^{++}]}$$

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that is, the potential set up depends partly on the oxidation-reduction ratio and partly on the hydrogen-ion concentration. E_0' is then a subsidiary standard giving the potential of the electrode when half the permanganate has been reduced in a solution of given hydrogen-ion concentration.

Examples of some standard oxidation-reduction potentials are given below.

System	Temp.	E_0'
$Ce^{++++} : Ce^{+++}(+ \text{dil. } HNO_3)$	17°	$+ 1.567$ V
$MnO_4^- + 8H^+ : Mn^{++} \ (N.H_2SO_4)$		$+ 1.45$
$Ce^{++++} : Ce^{+++} \ (+ \text{dil. } H_2SO_4)$	17°	$+ 1.431$
$Tl^{+++} : Tl^+ \ (+ 0.1N.H_2SO_4)$	18°	$+ 1.211$
$Fe^{+++} : Fe^{++}$ (weakly acid)	25°	$+ 0.743$
Quinone : hydroquinone $(+ 0.1N.HCl)$	18°	$+ 0.618$
$I_2 : 2I^-$	—	$+ 0.54$
$FeC_6N_6^{---} : FeC_6N_6^{----}$	25°	$+ 0.406$
$Cu^{++} : Cu^+$	—	$+ 0.18$
$Ti^{++++} : Ti^{+++} \ (+ 4N.H_2SO_4)$	18°	$+ 0.056$
$V^{+++} : V^{++} \ (+ N.H_2SO_4)$	18°	$- 0.204$
$Sn^{++++} : Sn^{++} \ (+ HCl)$	25°	$- 0.426$

Potentiometric Titration. As an example in which the concentration of the hydrogen-ion is concerned we may take the determination of ferrous iron with acid permanganate solution. In Fig. 1 (IX *) is shown the form
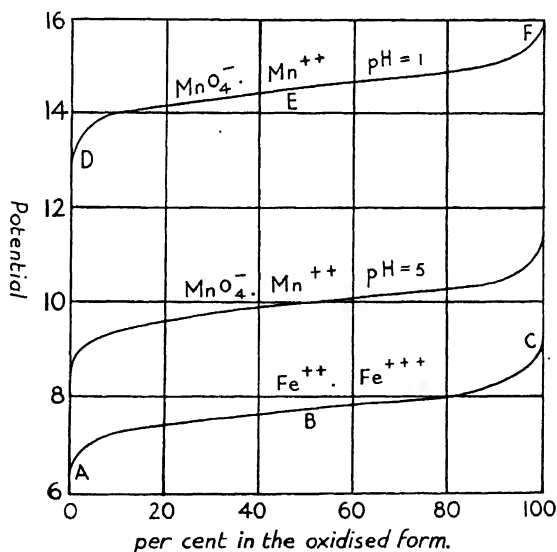
FIG. 1 (IX *)

of the oxidation-reduction curves for the substances involved in the reaction. These curves are calculated from the equations given above, using for the values of the standard oxidation-reduction potentials E_0'.

$Fe^{+++} : Fe^{++}$	0.77 volts
$MnO_4^- + 8H^+ : Mn^{++} \ (pH = 1)$	1.45 ,,
$MnO_4^- + 8H : Mn^{++} \ (pH = 5)$	0.99 ,,

for example, in the case of the iron curve the point A represents the potential of a platinum electrode in a solution nearly all in the ferrous condition; the point C the corresponding potential when the solution contains ferric ion with only a trace of ferrous. The point B half-way across the diagram gives the standard potential, 0·77 volt, i.e. that which the platinum plate would acquire in a solution containing equivalent amounts of ferrous and ferric ions.

If we start with a ferrous solution, a platinum electrode will give the voltage corresponding to A, and as we proceed to titrate with permanganate, the solution being normal with respect to sulphuric acid, the ratio ferric/ferrous will increase and the potential will follow the course of the curve ABC till all the ferrous has been converted into ferric. At this moment, which is the end-point of the titration, the solution contains no ferrous ion, much ferric ion, an equivalent amount of manganous ion (formed in the titration) and no permanganate. On the addition of the slightest
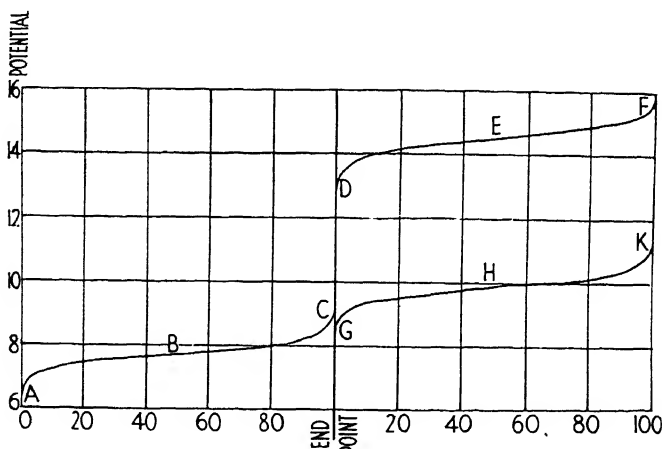
FIG. 2 (IX *)

trace of excess of permanganate we get the conditions represented by the point D in Fig. 1 (IX *), and the continued addition of permanganate will cause the potential to follow the curve DEF.

In Fig. 2 (IX *) the two parts of the diagram are placed side by side; the end-point of the titration is on CD and in this neighbourhood a single drop of the permanganate will give a large change of voltage. It is to be noted that the curve DEF refers to permanganate, in which the hydrogen-ion concentration is one. In both figures the curve GHK is the oxidation-reduction potential curve for permanganate in which the hydrogen-ion concentration is 10^{-5} ($pH = 5$), and it will be seen from the second figure that no marked jump in potential occurs at the end-point, so that this point could not be determined potentiometrically with this low acidity. We may take it that a difference of at least 0·3 volt is essential between the standard potential values of the two systems.

To carry out the experiment a measured quantity of the ferrous sulphate solution is acidified with sulphuric acid and placed in a beaker together

with a stirrer, a saturated calomel electrode and a bright platinum wire electrode : both electrodes are connected directly to a millivoltmeter. The solution is titrated quickly in the cold, the stirrer being stopped while the voltmeter is read. The following selected readings from an experiment on 20 ml. of a ferrous sulphate solution titrated with 0·0998 N. permanganate show the results obtainable :

ml. KMnO$_4$	Voltmeter	ml. KMnO$_4$	Voltmeter
0	0·304	18·5	0·900
10	0·410	18·6	0·930
15	0·440	18·9	0·955
18	0·500	20	0·980
18·2	0·520	25	1·023
18·35	0·552		

On plotting, this gives the end-point 18·48 ml., while the pink colour was first perceptible one drop later. The normality of the ferrous solution works out to 0·0922.

Oxidation-reduction Indicators. The most important of these are substances which give a reversible oxidation-reduction system to which the theoretical considerations apply which have been given above and in which also the oxidized and reduced forms are of different colours. In many cases the oxidized form is a highly coloured dyestuff and the reduced form the colourless leuco base. The indicators themselves could be titrated and would give curves similar to those in Fig. 2 (IX *) and corresponding to each change in the ratio oxidized form/reduced form there would be a change in potential and also a change in the depth of colour. Similarly the standard potential will be that given when the oxidized and reduced forms are present in equal amounts. The important point is that potentials are related to the depth of colour. In acid-base indicators the change is often in the nature of the colour, i.e. in its position in the spectrum ; but with oxidation-reduction indicators it is a change in intensity or depth of colour.

Now if, for example, we add a very minute amount of indicator to a ferrous-ferric system we shall have equilibrium set up according to the equation

$$Fe^{+++} + \text{Reduced indicator} \rightleftharpoons Fe^{++} + \text{Oxidized Indicator}$$
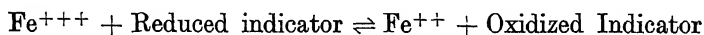
this will produce no appreciable change in the ratio Fe^{+++}/Fe^{++} because the amount of indicator added is so small, but the ratio for the indicator oxidized form/reduced form will be altered (perhaps considerably) until both systems have the same potential. So the indicator may be thought of as adjusting its potential to that of the ferrous-ferric system and since its colour is related to its potential, the colour would give the potential of the ferrous-ferric system provided that a suitable indicator had been chosen.

In a titration we want to find the point CD of the curve shown in Fig. 2 (IX *) where the potential is changing very rapidly. If we can find an indicator having its standard potential on CD this indicator will show practically the complete colour change from reduced form to oxidized form at the end-point.

If we take it that at C the ferrous salt is 99·9 per cent oxidized, the potential will be about 0·17 volt above the standard potential for the system : if the standard potential of the indicator is 0·05 volt or more above this we have secured the required conditions since a change from 90 per cent reduced indicator to 90 per cent oxidized indicator only requires a change of 0·12 volt and this, in the region CD, only corresponds to the addition of a single drop of the oxidizing agent.

Indicators of this kind are of particular value in cases such as when ceric sulphate is used as the oxidizing agent and there is no marked colour change. In titrating ferrous salts ($E_0 = + 0·77$ volt) with ceric sulphate ($E_0 = 1·60$ volts) xylene cyanole FF ($E_0 =$ about 1 volt) has been used.

The r_H Value. Where the oxidized and reduced states differ by two hydrogen atoms and when the substance is neither basic nor acidic in either the reduced or oxidized state we can proceed thus :

$$\text{Oxidized form} + 2H^+ + 2e \rightleftharpoons \text{Reduced form}$$
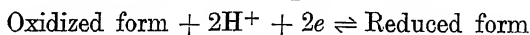
and
$$E = E_0 + \frac{RT}{2F}.\log_e\frac{[Ox.]}{[Red.]} + \frac{RT}{F}.\log_e[H^+]$$

for the hydrogen gas electrode with the gas at a pressure of P atmospheres we have the equation

$$E_H = \frac{RT}{2F}.\log_e\frac{1}{P} + \frac{RT}{F}.\log_e[H^+]$$

The hydrogen gas pressure required to give the same potential as the oxidation-reduction electrode will therefore depend on the values of E_0 and the ratio oxidized form/reduced form : these last two quantities determine the oxidation intensity of the system : this intensity can therefore be defined by a quantity which is related to the corresponding hydrogen gas pressure P by the relation $r_H = \log\frac{1}{P} = -\log P$, introducing this into the first of the two above equations and converting to ordinary logs

$$E = 2·302 \frac{RT}{2F}\Big)r_H + \frac{RT}{F}.\log_e[H^+]$$

$$= \Big(2·302 \frac{RT}{2F}\Big)r_H - \Big(2·302 \frac{RT}{F}\Big)pH$$

and at 17°
$$E = 0·029\ r_H - 0·058\ pH$$

hence
$$r_H = \frac{E}{0·029} + 2pH$$

Thus the indicator methylene blue has a value for E_0' of $+ 0·011$ volt at $pH = 7$

then its r_H is $\frac{0·011}{0·029} + 2 \times 7 = 14·4$

and its r_H range would be about one unit either way, i.e. from 13·4 to 15·4.

The r_H factor was originally introduced by Clark, but he now points out that it is only legitimate to use it in the case of the systems referred

to above : in the majority of cases this simple relationship between the potential and the pH value of the system does not hold and the use of the term should be discontinued.

Below is given a table of some of the more important oxidation-reduction indicators with their approximate working ranges.[1]

Indicator	E_0' at pH 7·0	Approximate r_H range
Barium diphenylamine-sulphonate		26–28
Benzyl-viologen	− 0·359	1–3
Bindschedler's green	+ 0·224	20·5–22·5
Brilliant cresyl blue	+ 0·047	15–17
o-Bromophenol-indophenol	+ 0·230	20–22
o-Chlorophenol-indo-2 : 6-dichlorophenol	+ 0·219	20–22
o-Chlorophenol-indophenol	+ 0·233	20–22
o-Cresol-indo-2 : 6-dichlorophenol	+ 0·181	18–20
m-Cresol-indophenol	+ 0·208	19–21
o-Cresol-indophenol	+ 0·191	18·5–20·5
Diphenylamine-sulphonic acid	—	26–28
Guaiacol-indo-2 : 6-dibromophenol	+ 0·159	17·5–19·5
Janus green	− 0·255	4·5–6·5
Lauth's violet (thionine)	+ 0·063	15–17
Methylene blue	+ 0·011	13·5–15·5
1-Naphthol-2-sodium sulphonate-indo-2 : 6- dibromophenol	+ 0·119	16–18
1-Naphthol-2-sodium sulphonate-indo-2 : 6- dichlorophenol	+ 0·118	16–18
1-Naphthol-2-sodium sulphonate-indophenol . . .	+ 0·123	16·5–18·5
Neutral red	− 0·325	2–4
Phenol blue	+ 0·224	20–22
Phenol-indo-2 : 6-dibromophenol	+ 0·218	20–22
Phenol-indo-2 : 6-dichlorophenol	+ 0·217	20–22
Phenol-indophenol	+ 0·227	20–22
Pheno-safranine	− 0·252	5–7
Potassium indigo-disulphonate	− 0·125	8–10
Potassium indigo-trisulphonate	− 0·081	9·5–11·5
Potassium indigo-tetrasulphonate	− 0·046	11–13
Rosinduline	− 0·281	3·5–5·5
Thymol-indophenol	+ 0·174	18–20
Tolylene blue	+ 0·115	16–18
m-Tolylenediamine-indophenol	+ 0·125	16·5–18·5

Method of Using Indicators. In titrations the method of using oxidation-reduction indicators is similar to that used in acidimetry and alkalimetry, where, for example, in titrating sodium hydroxide with an acid using phenolphthalein, the end-point is given by the disappearance of the pink colour. The titration of reducing sugars with Fehling's alkaline copper solution was modified by Lane and Eynon (1923) by the use of methylene blue as indicator. Previously the end-point was the disappearance of the

[1] The Colorimetric Determination of Oxidation Reduction Balance—from British Drug House Analytical Laboratories, 2nd ed. revised with additions, 1937. The above indicators have been specially prepared for oxidation-reduction work in the laboratories of The British Drug Houses. See B.D.H. Catalogues for prices.

last trace of the blue colour due to the copper ; with the addition of methy-lene blue the solution retains a deep blue colour up to the end-point, and then a very small excess of the sugar reduces the methylene blue to the colourless leuco base giving a much sharper end-point.

In some cases the indicators themselves may be used as volumetric reagents : an example is the use of phenol-indo-2 : 6-dichlorophenol as a volumetric reagent for the determination of ascorbic acid (Vitamin C), in acid solution the colour change is from red to colourless or very pale yellow and in neutral solution from blue to colourless or pale yellow.

Many of the indicators used for biological purposes, where the pH values are frequently in the neighbourhood of 7, are substances similar to the quinone-hydroquinone system where the potential is dependent on the pH value of the solution. What is done is to take a number of specimens of the solution under examination and try them with different indicators, so getting down to the limits in which one is reduced as shown by the colour change and the next in the series is not : if the pH of the solution is known, its potential can then be calculated.

The use of methylene blue in milk testing is well known [1] and another good example is Miller's method for determining the dissolved oxygen in water to test its capacity to deal with sewage effluents. A measured volume of water is buffered with alkaline tartrate, one drop of 0·05 per cent pheno-safranine added as indicator and the solution is titrated with ferrous sulphate till the colour of the indicator fades.

Oxidation-Reduction indicators receive very thorough treatment in *Newer Methods of Volumetric Chemical Analysis*.[2] This section (Part 6) is written by Bennecke and contains a bibliography of recent work in this very important field. Among the indicators considered are : diphenyl-amine, diphenylbenzidene, diphenylamine sulphonic acid, erioglaucin, eriogreen, setoglaucin, tri-ortho-phenanthroline, ferrous sulphate and many related products.

[1] Grimes, Barrett and Reilly, ' Methylene Blue (Reductase Test) in Milk Grading,' *Sci. Proc. Roy. Dubl. Soc.*, 1927, *18*, 437.
[2] Edited by Bottger, Chapman and Hall, 1938.

CHAPTER X *

THERMIONIC VACUUM TUBES

APPLICATIONS OF THERMIONIC VACUUM TUBES [1]

WHEN a conductor is heated electrons are emitted. This thermionic emission, as it has been called by O. W. Richardson,[2] who was the first to conduct a thorough investigation on the subject, originates from the free electrons which exist in the conductor, and the rate at which the electrons escape from the surface depends on the velocity distribution of the electrons in the body and on the repulsive forces existing at the surface. As the temperature of the conductor increases an increasing proportion of the electrons reach the surface with velocities sufficient to overcome these repulsive forces and the thermionic emission increases.

It has been shown by Richardson and others [3] that the emission per unit area of the surface of an emitter at a temperature T° K can be represented by the equation

$$i_s = AT^2 e^{-\frac{b}{T}}$$

where A and b are constants for a given material.

The velocities of the emitted electrons are distributed according to Maxwell's velocity distribution law applied to an electron gas having the temperature of the emitter. At temperatures at which thermionic emitters normally operate the average energy of the electrons is only a small fraction of an electron volt [4] and for most practical purposes it is sufficiently accurate to assume that the emission velocity is zero.

Tungsten was one of the earliest emitting materials used, on account of its high melting-point and its low vapour pressure at temperatures at which it gave a useful emission. Thoriated tungsten (tungsten containing about 1 per cent thoria) was later found by Langmuir [5] to give a greater emission than pure tungsten, and it has been shown that this is due to a thin film of thorium, about one atom thick, which forms on the surface when the thoriated tungsten is heated to a high temperature. Some of the thoria is reduced, the oxygen is liberated and thorium diffuses to the surface.

[1] Revised and re-written by G. W. Warren, B.Sc., a member of the Research Staff of the General Electric Co., Ltd., and of the M.O. Valve Co., Ltd., Wembley.

[2] *Phil. Trans. Roy. Soc.*, 1903, *201*, 497.

[3] Reimann, *Thermionic Emission* (Chapman and Hall), 1934.

[4] One electron volt (eV) is the energy acquired by an electron in falling through a potential difference of one volt.

[5] *Phys. Rev.*, 1923, *22*, 357.

In most small modern thermionic tubes the ' oxide coated ' emitter is used, which consists of a nickel core coated with a thin layer of a mixture of barium and strontium oxides. The nickel is first coated with a solid solution of barium and strontium carbonates [1] which decompose to the oxides when heated *in vacuo*, and the emitter is activated by further heating at about 1,150° to reduce some of the barium oxide to barium, which forms the emitting film on the surface. A trace of some reducing agent such as aluminium, magnesium, or silicon in the nickel enhances the emission considerably.[2] The following table gives the approximate operating temperature, emission per unit area and efficiency as measured by the emission per watt supplied to the emitter for these three types of emitting surface :

Emitter	Operating Temperature	Emission mA per cm.^{2}	Efficiency mA per watt
Tungsten . . .	2,500° K	275	4
Thoriated Tungsten	1,900	1,000	55
Oxide coated . .	1,050	250	250

Tungsten and thoriated tungsten emitters are used as cathodes in thermionic tubes in the form of a wire which can be heated by an electric current. Oxide-coated cathodes may, however, on account of their lower operating temperature, be either directly heated by a current or indirectly heated by radiation and conduction from a separate heater. In the latter case the cathode is usually in the form of a tube which surrounds and is insulated from a heater of a refractory metal, such as tungsten, the insulating material being aluminium oxide of very high purity. Indirectly heated cathodes are used when it is desired to heat the cathode with power from the supply mains, either direct or alternating current, without introducing fluctuations in the thermionic current due to the varying electric and magnetic fields of the heating supply.

The emitting properties of cathodes, particularly of the thoriated tungsten and oxide-coated types, are extremely sensitive to small traces of certain gases. All the components of thermionic vacuum tubes are therefore freed from adsorbed gases by heat treatment while the tube is being exhausted, and a final pressure of less than 10^{-7} mm. of mercury is obtained by dispersing a ' getter ' film of magnesium or barium on the walls of the bulb.

Diodes. The simplest type of thermionic vacuum tube, or valve, is a diode (Fig. 1 (X *)) consisting of a thermionic cathode, C, and an anode, A, in an evacuated envelope. The electron current from the cathode to the anode in such a tube depends not only on the temperature of the cathode but also on the potential (V) of the anode relative to the cathode. When V is negative the value of the space current will be negligible, since only those electrons which are emitted with high velocities will be able to reach

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[1] Benjamin and Rooksby, *Phil. Mag.*, 1933, *15*, 810, and *16*, 519.
[2] Benjamin, *Phil. Mag.*, 1935, *20*, 1.

the anode. As V becomes positive the electron current will increase as shown in Fig. 2 (X *) until a voltage, V_s, the saturation voltage, is reached above which the current will remain almost constant at the value of the total emission from the cathode. When V is less than V_s the thermionic current is limited by the negative space charge due to the electrons between the cathode and anode and is independent of the temperature of the cathode. Thus, if the temperature of the cathode is increased, or if a cathode of equal size but having better emitting properties is substituted, the current voltage relationship will be given by a curve such as OABEF (Fig. 2 (X *)), the portion of the curve OAB being unaffected, although the saturation voltage and saturation current will be increased.
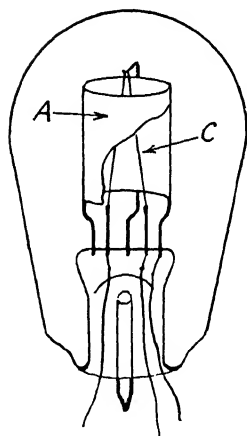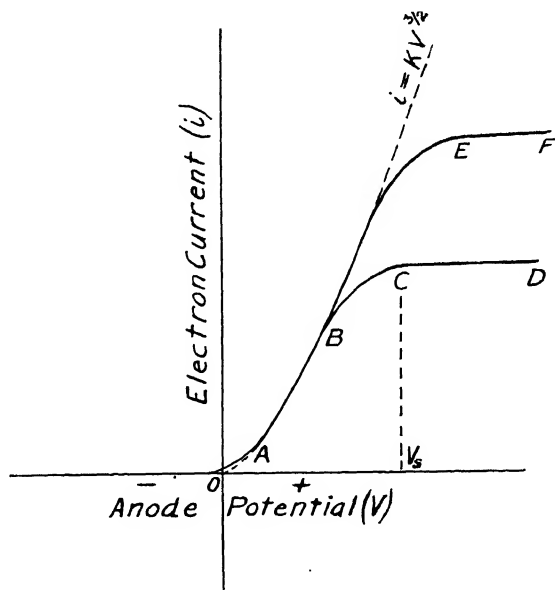
FIG. 1 (X *)   FIG. 2 (X *)

The physical meaning of a space-charge-limited current is simply that the positive charge on the anode at any instant exactly equals the total negative charge of the electrons in the space between the electrodes, with the result that the electric field or potential gradient at the cathode surface is zero. Variations of the anode potential vary the field at points near the cathode surface and therefore cause a change in the space current.

It can be shown theoretically [1, 2] that the value of the space-charge-limited current in a diode should obey an equation of the form

$$i = KV^{3/2}$$

where K is a constant depending only on the geometry of the electrode system. The characteristics of diodes do, in fact, obey a three-halves-power law over a considerable portion (AB) of the curve, and, with few exceptions, vacuum tubes operate under this condition. Deviations from

Child, *Phys. Rev.*, 1911, *32*, 498.   [2] Langmuir, *Phys. Rev.*, 1913, *2*, 450.

the three-halves-power law occur at the lower end (OA) of the curve due to the effect of the initial velocities of the electrons, and at the upper end (BC) owing to the effect of end cooling of the cathode and irregularities in the cathode surface.

The resistance of a diode to alternating current is given by the reciprocal of the slope of the characteristic curve, so that over the portion AB this will be

$$r_a = 1 \bigg/ \left(\frac{di}{dV}\right) = \frac{2}{3KV^{1/2}}$$

Diode Rectifiers. The principal application of diodes is in the rectification of alternating currents, as, for example, when a D.C. supply is required from A.C. mains. Since the electron current only flows when the anode is positive with respect to the cathode, if an alternating potential is applied to the anode (Fig. 3 (X *)) the current at any instant can be

FIG. 3 (X *)

(a) Input voltage   (b) Electron current
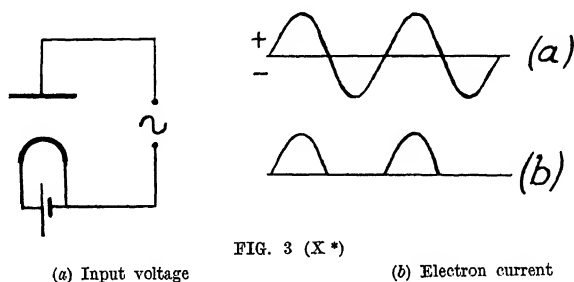
determined from the diode characteristic and the wave form of the current will be as shown in Fig. 3 (X *) b. If there is a load of resistance, R, in series with the diode (Fig. 4 (X *)), then the current at any instant will be given by the ordinate of the point of intersection with the diode characteristic of a line whose slope is $-\frac{1}{R}$ drawn from the point X, where OX represents the instantaneous value of the applied voltage (Fig. 4 (X *) a).
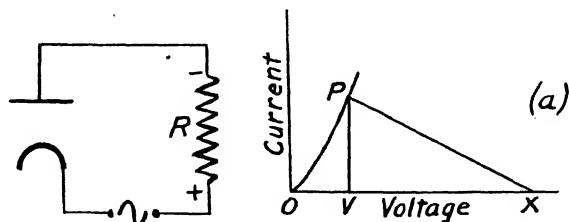
FIG. 4 (X *)

This graphical method of representing the current/voltage relationship in a valve circuit is extremely useful, since it shows at once the value of the current (VP), the voltage across the valve (OV) and the voltage across the load (VX) for any value of applied voltage (OX) and load resistance (VX/VP). If a large condenser, C, is connected across R this condenser

will charge up during the positive half-cycles to a potential approaching
the peak value of the voltage
across R, and discharge through
R during the negative half-cycles
so that there will be a continuous
current in the load (Fig. 5 (X*)).
By inserting in series with the load
an inductance whose D.C. resist-
ance is small but whose impedance
at the frequency of the alternating
supply is large, the output current
and voltage can be smoothed to
any required degree.

A better method of rectification
employs two diodes arranged as in
Fig. 6 (X*), the output being
obtained between the centre point
of the input supply (e.g. the
secondary winding of a trans-
former) and the cathodes. Current
flows in the load alternately from
each diode every half cycle so that the

FIG. 5 (X*)
Half-wave Rectifying Circuit
(a) Input voltage   (b) Output voltage across R

output current wave form is as
shown in Fig. 6 (X*) a. This
full wave rectification possesses
the advantage that smaller con-
densers and chokes are required
to smooth out the alternating
component of the output than
in half-wave rectifiers. Rectify-
ing valves containing two diodes
in a single envelope with the
two filaments connected in series
or in parallel are frequently
employed.

Fig. 7 (X*) shows a circuit
in which two diode rectifiers can
be used to obtain a D.C. output
of approximately twice the volt-
age of an A.C. supply, the two
condensers being charged in
series alternately from each
diode every half-cycle.

Diode Voltmeters. A diode
may also be used to measure
alternating voltages. The volt-
age to be measured is applied
to the valve in series with a

FIG. 6 (X*)
Full-wave Rectifying Circuit
(a) Output voltage across R condenser and inductance
(b) Smoothed output

condenser, which therefore charges to the peak value of the input. The
steady voltage across the condenser can be measured by an electrostatic

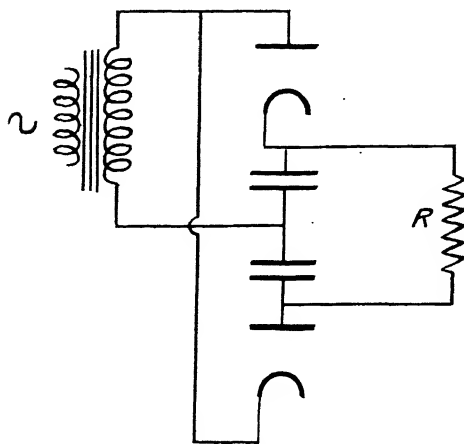voltmeter or by a microammeter in series with a very high resistance shunting the condenser or by potentiometer. For low voltages the potentiometer arrangement (Fig. 8 (X *) e) is the best. The slider, S, is moved in the direction PQ until the current in the galvanometer, G, just ceases to flow, at which point the voltmeter, V, reads the peak voltage applied. Diode peak voltmeters are particularly useful for measurements at high (radio) frequencies owing to their low capacity. More detailed discussion of the diode peak voltmeter will be found in papers by Paterson and Campbell,[1] Bartlett,[2] and Megaw.[3]

FIG. 7 (X *)
Voltage doubling circuit

Triodes. Probably the most important development in the history of the thermionic vacuum tube was made in 1907 by de Forest, who found that the electron current from cathode to anode could be controlled by potentials applied to a third electrode, the grid, in the form of a wire helix or mesh placed between the cathode and the anode. This increased the range of usefulness of thermionic valves considerably, not only in the field
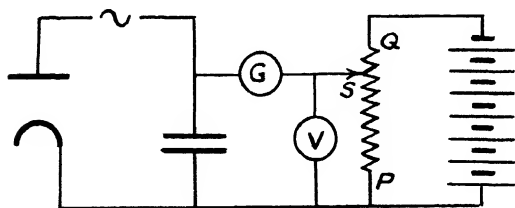
FIG. 8 (X *)
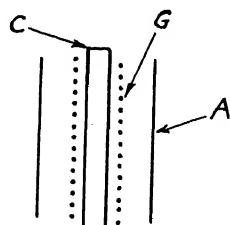
FIG. 9 (X *)

of radio communication, but also in their applications to physical and physico-chemical problems. The manner in which the grid of a triode controls the current was first explained by Van der Bijl,[4] and the theory has since been developed further by Schottky[5] and others.

If C, G, and A (Fig. 9 (X *)) represent the cathode, grid, and anode of a triode, the potential distribution in the neighbourhood of the cathode, and therefore the cathode current, will depend on the potentials of the anode and grid relative to the cathode, and the grid will act as an electrostatic screen which will reduce the effect of the anode potential on the potential near the cathode.

[1] *Phil. Mag.*, 1919, *37*, 301.　　　　　　　　　[2] *J. Sci. Inst.*, 1924, *1*, 281.
[3] *Wireless Engineer*, 1936, *13*, 65, 135 and 201.
[4] *Verh. D. Phys. Ges.*, 1913, *15*, 338, and *Phys. Rev.*, 1918, *12*, 180.
[5] *Arch. Elektrotechnik*, 1919, *8*, 1 and 12.

If e_g and e_a are the potentials of the grid and anode respectively and the cathode current is changed by increasing the anode potential by an amount δe_a, the current can be restored to its original value by altering the grid potential by an amount

$$- \delta e_g = \frac{\delta e_a}{\mu}$$

where μ is a constant (usually greater than unity) for a given electrode system.

This constant, μ, which gives a measure of the screening of the cathode from the anode by the grid, is known as the amplification factor of the triode and its value depends on the closeness of the grid spiral or mesh and on the distance between the grid and anode.

It can be shown from electrostatic considerations that the potential distribution near the cathode surface, and therefore the space current, in a triode is the same as that in a diode whose anode is placed in the position occupied by the grid of the triode and given a potential

$$e_d = \frac{e_g + \dfrac{e_a}{\mu}}{1 + \dfrac{1}{\mu}}$$

Since the space-charge-limited current in this 'equivalent diode' is

$$i = K e_d^{3/2}$$

it follows that the current in the triode is given by

$$i = K \left\{ \frac{e_g + \dfrac{e_a}{\mu}}{1 + \dfrac{1}{\mu}} \right\}^{3/2}$$

When the grid is at a negative potential relative to the cathode the whole of the electron current flows to the anode.
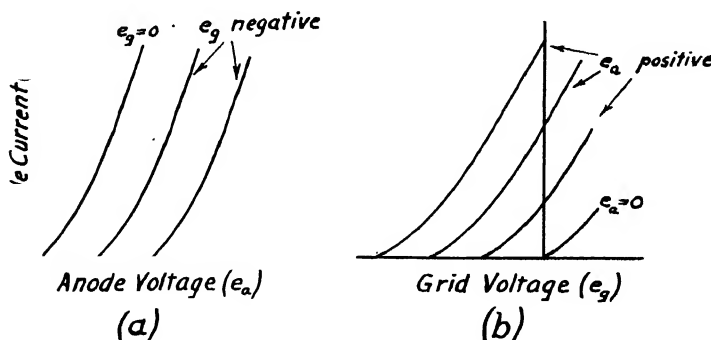
FIG. 10 (X *)

The above equation for the anode current of a triode can be represented by either of two families of curves, anode current plotted against anode voltage for different fixed values of grid voltage (Fig. 10 (X *) a), or anode

current plotted against grid voltage for different values of anode voltage (Fig. 10 (X *) b).   Each of these curves is similar in shape to a diode characteristic displaced horizontally, in Fig. 10 (X *) a by an amount $- \mu e_g$ from the curve corresponding to $e_g = 0$, and in Fig. 10 (X *) b by an amount $- \dfrac{e_a}{\mu}$ from the curve corresponding to $e_a = 0$.   The slope (di/de_a) of the anode-current/anode-voltage curve gives the A.C. conductance $(1/r_a)$ of
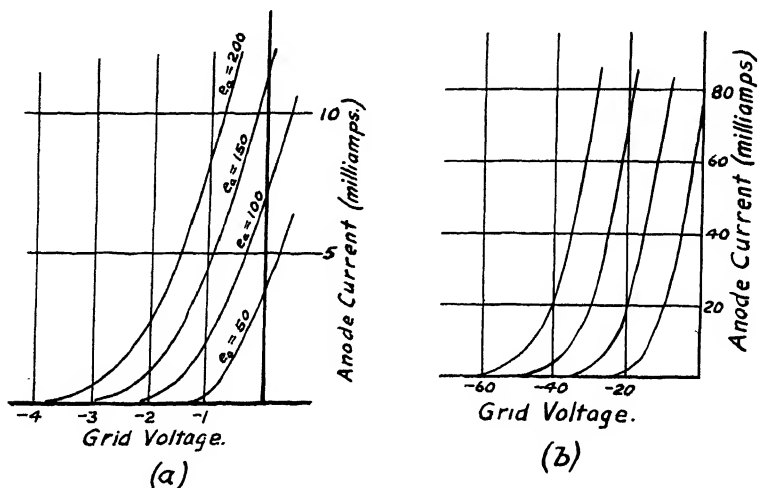

FIG. 11 (X *)

(a) Anode Current Grid Voltage Characteristics for valve with high amplification factor ($\mu = 80$)
(b) Ditto for valve with low amplification ($\mu = 9 \cdot 5$)

the valve and the slope (di/de_g) of the anode-current/grid-voltage curve is known as the mutual conductance (g_m), an important quantity which for many purposes measures the efficiency of the valve.

In practice the approximation to the three-halves-power law is not quite so close in a triode as it is in the case of a diode, and Fig. 11 (X *) shows the actual characteristics of typical triodes having high and low amplification factors.

Triode Oscillators. For many physical and physico-chemical measurements, for example, in the determination of the conductivity or dielectric constants of electrolytes,[1, 2, 3] a source of alternating current at audio or radio frequency is required, and for this purpose a triode valve oscillator is usually employed.

A tuned circuit consisting of an inductance and condenser will oscillate at a frequency

$$f = \frac{1}{2\pi\sqrt{\text{L.C.}}} \text{ cycles per second}$$

where L is the inductance of the coil in henrys, and C is the capacitance of the condenser in farads.   The coil, however, always has some resistance

[1] Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, A, *123*, 664.
[2] Ball, *J. Chem. Soc.*, 1930, 576.   [3] Sugden, *J. Chem. Soc.*, 1933, 768.

and therefore dissipates energy in the form of heat, so that oscillations, once started, will rapidly die away. The triode affords a means of supplying to the oscillating circuit the energy dissipated due to its resistance or any other load imposed on the circuit. Fig. 12 (X *) shows one method of doing this. The tuned circuit (L.C.) is connected between the grid and cathode in series with a battery which brings the grid to a suitable mean negative potential. An inductance, L_a, in the anode circuit is coupled to the oscillator coil, L, in such a way that an increase in the current in L_a
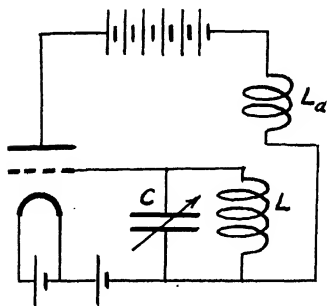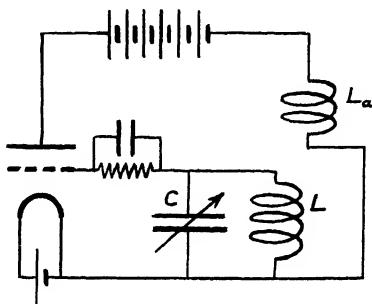
FIG. 12 (X *)   FIG. 13 (X *)

induces an E.M.F. in L which makes the grid more positive, while a decrease in the anode current induces an E.M.F. which makes the grid more negative. Energy is thus fed back from the anode to the grid circuit and an unstable condition, resulting in continuous oscillation, is reached when the energy fed back exceeds the total losses in the oscillating circuit. It will be obvious that the higher the mutual conductance ($g_m = di/de_g$) of the valve the more readily will the circuit oscillate. The amplitude of the oscillating voltage across the circuit LC will be limited by the load imposed by grid current when the grid becomes positive and the reduction in mutual conductance when the grid swings to a high negative potential.

It is usual to employ a grid leak and condenser in parallel [1] instead of a grid-bias battery (Fig. 13 (X *)). When the grid first swings positive electrons

FIG. 14 (X *)
Valve Oscillator (Hartley Circuit)

are collected which only leak away slowly through the resistance and the grid is self-biased to a potential near the cut-off point of the anode-current/grid-voltage curve. Fig. 14 (X *) shows an alternative oscillator which is frequently used.

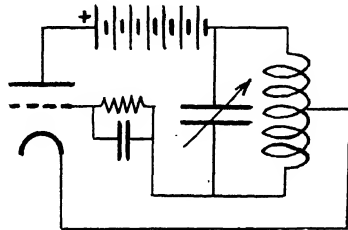When a very constant frequency is essential, tuning-fork or crystal

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[1] The best values of resistance and capacitance of the leak and condenser will depend on the frequency and power required. A more exhaustive treatment of the subject will be found in textbooks on Radio Engineering, e.g. see:—
Terman, *Radio Engineering* (McGraw-Hill Book Co.), 1937.

controlled oscillators can be employed (for audio or radio frequencies respectively).

In the tuning-fork controlled oscillator (Fig. 15 (X *)) the magnetic field of the oscillator coil, which may be tuned approximately to the frequency of the fork (although this is not necessary), maintains the vibrations of the fork which, in turn, determines the frequency of the oscillating current in the circuit.
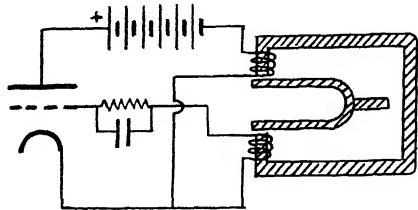
FIG. 15 (X *)

The operation of the crystal controlled oscillator depends on the piezo-electric properties of the crystal, quartz being the most commonly used. The natural resonant frequency of the mechanical vibration of the crystal depends on its dimensions and on the way in which it is cut. The oscillating potential developed as the result of the mechanical vibration is applied to the grid of the triode and, as in the tuning-fork controlled oscillator,
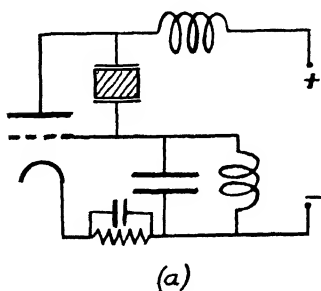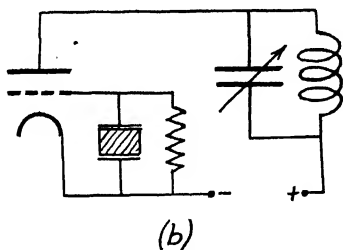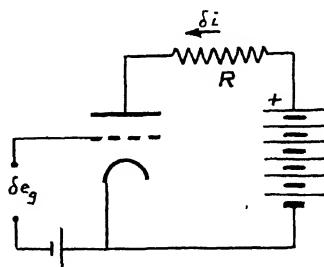
(a)   (b)

FIG. 16 (X *)

the energy required to maintain the vibrations is supplied by the valve. In Fig. 16 (X *) are shown two simple circuits which employ a quartz crystal to control an oscillator; in the first example (a) the energy is fed back from anode to grid through a condenser having the crystal as its dielectric, and in the second example (b) the reaction is provided by the anode-grid capacitance of the valve itself. By suitably cutting the crystal any constant frequency between about 50 and 2,000 kilocycles per second may be obtained.

Triode Amplifiers. An important application of the triode is in the amplification of small steady or alternating potentials (or currents).

When the grid potential is altered by a small amount, δe_g, the anode current will

FIG. 17 (X *)
Single-valve Amplifier

change by an amount δi and this will produce a change in the potential across the resistance, R, in the anode circuit of value $\delta e_a = - R \delta i$ (Fig. 17 (X *)).

Now, since $i = f(e_a, e_g)$ $\qquad$ $\delta i = \dfrac{di}{de_a}\delta e_a + \dfrac{di}{de_g}\delta e_g$

$$\therefore \; \delta e_a = -\mathrm{R}\delta i = -\mathrm{R}\left\{\dfrac{di}{de_a}\delta e_a + \dfrac{di}{de_g}\delta e_g\right.$$

$$= -\mathrm{R}\left(\dfrac{1}{r_a}\delta e_a + g_m\delta e_g\right)$$

and $\because g_r - \dfrac{\mu}{}$ $\qquad$ $e_a\left(1 + \dfrac{\mathrm{R}}{r_a}\right) = -\dfrac{\mu\mathrm{R}}{r_a}\delta e_g$

So that the voltage amplification $\dfrac{\delta e_a}{\delta e_g} = -\dfrac{\mu\mathrm{R}}{\mathrm{R} + r_a}$

the minus sign indicating that the amplified voltage is 180° out of phase with the input.

The above result is obtained by regarding the input voltage δe_g to the grid as being equivalent to an E.M.F. whose value is $\mu.\delta e_g$ applied to a circuit containing the anode resistance r_a in series with the output resistance R. The voltage developed across R will then be

$$\delta e_a = \dfrac{\mu.\delta e_g.\mathrm{R}}{\mathrm{R} + r_a}$$

from which it follows that the amplification is

$$\dfrac{\mu.\mathrm{R}}{\mathrm{R} + r_a}$$

As R approaches infinity the amplification approaches μ, the amplification factor of the valve. At the same time, however, the anode current approaches zero, and the maximum useful amplification will, in practice, depend on the power required in the output circuit.

When the input potential is alternating, the load in the anode circuit may be an inductance (either a choke or the primary winding of a transformer) whose impedance is high at the frequency of the alternating current but which has a low D.C. resistance. The amplification can thus be made to approach the amplification factor of the valve with an appreciable D.C. current flowing without applying an excessive voltage to the anode circuit and wasting power in the load.

When more than one stage of amplification are required the amplified voltage across the output load of the first valve is applied to the grid of the second valve. The grid of this valve must, however, be maintained at a negative potential with respect to its cathode, and in A.C. amplifiers this condition is met by feeding the alternating potential from the first anode to the second grid through a condenser having a reactance which is low compared with the output load R. Alternatively, the valves may be coupled by means of a transformer. Methods of coupling successive stages of a multi-stage amplifier are shown in Fig. 18 (X *). In D.C. amplifiers these methods cannot be used and, in order to keep the grid of the second valve at a negative potential, it is necessary to insert a battery between anode and grid as shown in Fig. 19 (X *). Another method often employed

is to interrupt the D.C. input to the amplifier by means of a rotating commutator, when an A.C. amplifier can be used, the output from which is rectified.
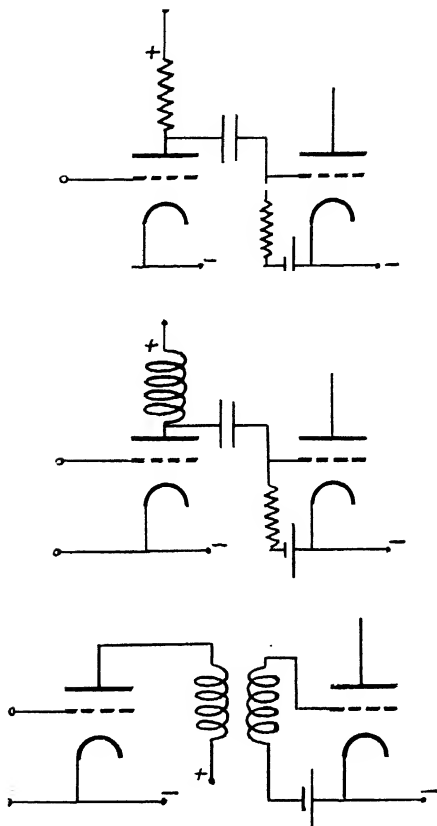
Triode Voltmeters. The very high resistance between the grid and cathode of a triode when the grid is at a negative potential renders it extremely useful as a voltmeter which imposes only a very small load on the source of potential to be measured. A further advantage of the valve voltmeter lies in the fact that it can be used for measuring alternating voltages at frequencies quite outside the range of the electromagnetic type of instrument.

In the simplest case the value of a steady voltage applied between grid and cathode is measured by observing the change in anode current, the anode-current/grid-voltage characteristic having first been determined. In order to measure small changes in the anode current the normal current flowing before the application of the unknown voltage to the grid may be balanced out of the meter by a simple circuit consisting of a cell of voltage, E, and a resistance, R, arranged as shown in Fig. 20 (X *). If i is the normal anode current, no current will flow in the meter when $E = -iR$. In another method the unknown potential is applied to the

FIG. 18 (X *)
Methods of Coupling used in A.C. Amplifiers
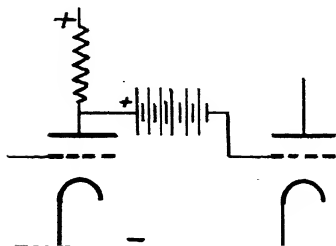
FIG. 19 (X *)
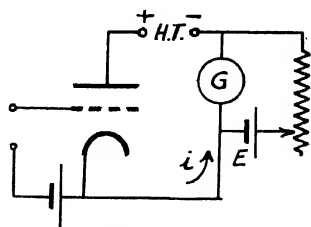Inter-valve Coupling in D.C. Amplifier

FIG. 20 (X *)
Valve Voltmeter

grid in opposition to the voltage from a potentiometer, which is adjusted until the anode current is restored to its original value (Fig. 21 (X *)).

No calibration of the valve is, in this case, necessary, the potential being measured on the potentiometer.

Since the anode-current/grid-voltage curve is not straight, but is concave upwards, the former of the above methods may be used to measure alternating voltages, the application of which to the grid will result in an increase in the mean value of the anode current. The instrument can be calibrated at a convenient frequency (say, 50 cycles per second) and the calibration will be independent of frequency over a wide range.

A more sensitive form of voltmeter for alternating voltages [1] is shown in Fig. 22 (X *). The alternating potential is applied to the grid through a condenser, C, whose capacitance is large compared with that between the valve electrodes, and a high resistance, R, of two or three megohms,
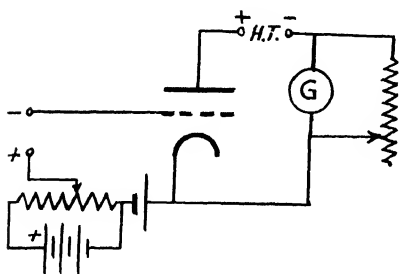

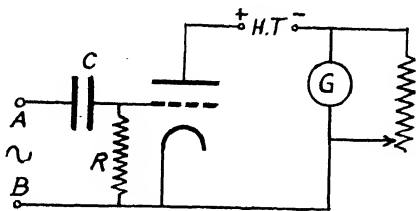FIG. 21 (X *)
Valve Voltmeter for D.C

FIG. 22 (X *)

is connected between grid and cathode. When no alternating potential exists across the input terminals AB, then, owing to the small but finite velocities of the electrons, the grid acquires a small negative potential, of the order of a volt, at which electrons reach the grid at the same rate as they leak back through R to the cathode. When an alternating potential is applied to AB the grid collects more electrons during the positive half-cycles, and since this charge only leaks back slowly through R, the time constant of the circuit CR being large compared with the period of oscillation of the input, the mean grid potential becomes more negative and the anode current decreases.

Modifications to the above simple circuits, with a view to improving the accuracy and stability of valve voltmeters, have been suggested by Medlan and Oschwald [2] and by Moullin.[3] The measurement of small currents, either A.C. or D.C., may be effected by measuring the voltage developed across a known high resistance when the current passes through it.

Electrometer Valves. Although the grid current in standard types of valve, when the grid potential is negative, is for most purposes negligible, it is not sufficiently small to allow the valves to be used for electrostatic measurements or for the measurement of currents less than about 10^{-8} amps. without elaborate compensating circuits. Special types, known as electrometer valves, have, however, been developed in which the causes

[1] Moullin, *J. Inst. Elec. Eng.*, 1923, *61*, 295.
[2] *Exp. Wireless*, 1926, *3*, 589 and 664.   [3] *J. Inst. Elec. Eng.*, 1928, *66*, 886.

of grid current, such as leakage, positive ions and photoelectric emission, have been eliminated as far as possible, with the result that the grid current under suitable operating conditions is as low as 10^{-16} amps.[1, 2]

One type of electrometer valve is a triode in which the anode and control electrode are in the form of two parallel plates with the filamentary cathode between them.[2] The amplification factor is rather less than unity, and the mutual conductance about 40 microamps. per volt, the anode operating at less than 6 volts. In another type, developed in America,[1] the grid and anode are of conventional design, but an auxiliary grid, to which a fixed positive potential is applied, is placed between the cathode and control grid. The purpose of the auxiliary grid, the ' space-charge grid,' is to reduce the impedance of the valve by overcoming the effect of space charge near the cathode and to prevent positive ions from the filament which is of tungsten, reaching the control grid.

The electrometer triode possesses certain advantages over other forms of electrometer, chief amongst which are greater sensitivity, robustness and low capacitance (about 2 micromicrofarads). One of the most important applications is in the measurement of glass electrode potentials in the determination of hydrogen-ion concentrations. The method was suggested by Harrison[3] and has been developed further by Morton[4] who, by eliminating the effects of small fluctuations in battery voltages, has made possible the construction of continuously recording instruments.

Electrometer triodes have also been used for the measurement of small ionization currents,[5] and for photometric measurements. In the latter case a photoelectric cell is used in conjunction with the triode, the current in the cell resulting from the illumination of the photoelectric surface being passed through a high resistance of between 10^8 and 10^{10} ohms, and the voltage across this resistance is applied between the grid and cathode of the valve. In order to minimize surface leakage the photo cell, grid resistance, and triode may be assembled in an evacuated envelope.[2] The output from the electrometer triode may, if necessary, be amplified by one or more stages containing high amplification valves.

Tetrodes. The capacitance between grid and anode of a triode is a disadvantage in amplification at high frequencies. This has led to the development of tetrode valves in which a screen, in the form of a closely woven mesh or grid of close pitch, is placed between the anode and control grid. This additional grid, which is operated at a fixed positive potential, screens the anode from the cathode, so that the cathode current is practically independent of the anode voltage over a wide range. Fig. 23 (X *) shows the anode-current/anode-voltage characteristics of a typical screen grid valve for a fixed-screen voltage and different values of control-grid voltage. With the anode voltage zero the cathode current flows into the screen. When the anode becomes positive the electrons which pass through the screen mesh strike the anode. The anode current rises steeply, and were it not for the emission of secondary electrons, would saturate as shown

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[1] Metcalfe and Thompson, *Phys. Rev.*, 1930, *36*, 1489.
[2] Warren, *G.E.C. Journal*, 1935, *6*, 118.   [3] *J. Chem. Soc.*, 1930, 1528.
[4] *Ibid.*, 1931, 2977, and 1932, 2469, and *J. Sci. Inst.*, 1932, *9*, 289.
[5] Benjamin, Cosgrove and Warren, *J. Inst. Elec. Eng.*, 1937, *80*, 401.

by the dotted curve. The secondary electrons emitted from the anode, under bombardment by the electrons from the cathode, are, however, accelerated towards the screen when the anode voltage is lower than that
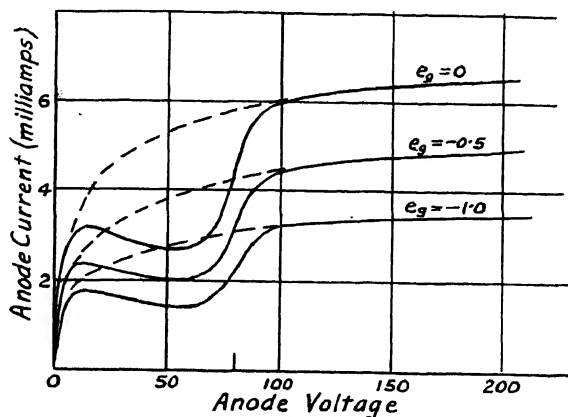

FIG. 23 (X *)

Tetrode (Screen Grid) Valve characteristics.

Screen potential = 80 volts
Amplification factor = 1200

of the screen, and secondaries from the screen flow to the anode when its potential is higher than that of the screen, with the result that the characteristics are as shown by the full lines.

Apart from the low anode-to-grid capacitance an important advantage of the screen grid valve is its high amplification factor, which may be as high as 3,000, a figure which cannot be obtained in triodes having any appreciable efficiency.

When used as an amplifier the screen grid valve is operated with the anode at a higher voltage than the screen. A convenient form of oscillator is, however, made possible

FIG. 24 (X *)

Tetrode (Dynatron) Oscillator

by operating the valve with the anode potential lower than the screen potential, where the anode conductance is negative, and with an oscillating circuit in series with the anode. Oscillations will be maintained if the negative conductance of the valve is sufficiently great. (Fig. 24 (X *)).

Pentodes. By suitably designing the tetrode it is possible to create sufficient space charge between anode and screen to suppress the secondary currents and the characteristics of such a tetrode will be as shown by the dotted curve of Fig. 23 (X *). An alternative method is used in the pentode valve. Here, an extra grid, at zero potential, is placed between the screen and anode which reduces the space potential sufficiently to prevent the flow of secondary electrons while allowing the primary electrons which have been accelerated by the high screen voltage to reach the anode.
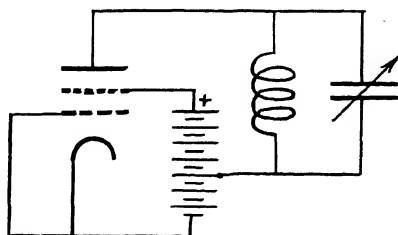
Other Types of Multi-electrode Valve. Valves having more than five electrodes and various multiple valves are in common use in radio receivers ; but their application is at present limited to this field and they need not be considered in this chapter.[1]

Secondary Emission Tubes. All materials emit secondary electrons when bombarded by electrons and in the case of certain suitably treated metals and metal oxides as many as nine or ten secondaries are emitted per primary electron when the latter strike the surface with velocities of a few hundred volts.

Thermionic valves, in which the secondary emission from the surface of an electrode, instead of being suppressed as in the pentode, is utilized with a view to improving the characteristics, have been suggested ; but these tubes are still in the experimental stage.

Photoelectric cells whose sensitivity is increased by amplification of the current at a secondary emitting surface have been developed, and Zworykin [2] has recently described a secondary emission multiplier, in which small currents from a photoelectric surface are multiplied several thousand times by successive amplification at a number of electrode surfaces (coated with an activated caesium oxide layer) each of which is operated at a higher potential than the one before it.

Gas-filled Tubes. If an inert gas or vapour is introduced at a low pressure into a thermionic tube, positive ions are produced when the anode voltage exceeds the ionization potential of the gas. The effect of the negative space charge due to the electrons is therefore reduced and the anode current saturates at a much lower voltage than it would in a vacuum tube of the same design.
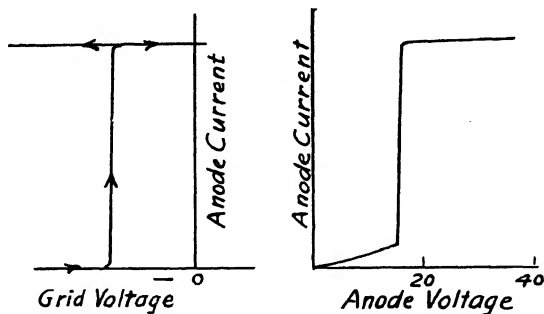

FIG. 25 (X *)

Diode rectifying valves containing a small quantity of mercury, the vapour pressure of which, at the operating temperature of the valve, is about 0·01 mm. of mercury, are frequently used when rectified currents of large magnitude are required. On account of the low resistance of such tubes there is only a small potential drop between cathode and anode and almost the whole of the output energy is dissipated in the load (see Fig. 4 (X *) a).

In gas-filled triodes the characteristics are as shown in Fig. 25 (X *).

[1] Benjamin, Cosgrove and Warren, *J. Inst. Elec. Eng.*, 1937, *80*, 401.
[2] *J. Inst. Elec. Eng.*, 1936, *79*, 1.

With the anode at a positive potential, above the ionization potential of the gas, if the grid is initially at a high negative voltage no current flows in the valve. When the negative potential on the grid is reduced, as soon as anode current starts to flow the gas is ionized and the current immediately rises to its saturation value. The positive ions flowing to the cathode and to the grid create a positive space charge which neutralizes the electrostatic field due to the grid. This electrode is, therefore, no longer able to control the anode current, which can only be stopped by reducing the anode voltage to a value below the ionization potential of the gas. The characteristics of gas-filled triodes render these tubes extremely useful as relays. Very large power in the output circuit can be controlled, while the energy in the grid circuit necessary to initiate the discharge is practically zero.

CHAPTER XI *

ELECTROLYTIC CONDUCTIVITY

SECTION 1 : TRANSPORT NUMBERS

INTRODUCTION. The transference number or transport number of any one ionic constituent of a substance is the ratio of the number of equivalents of this ion transferred to one electrode, to the arithmetical sum of the total number of equivalents of all the ions transferred to or from this electrode. If an electrolyte contains positive ions B′, B″, &c., and negative ions A′, A″, &c., and the equivalents of these ions transferred to the cathode are $N_{B'}$, $N_{B''}$, $N_{A'}$, $N_{A''}$, &c. the transference number of the constituent B′ is $T_{B'}$ where

$$T_{B'} = N_{B'}/(N_{B'} + N_{B''} \ldots \ldots + N_{A'} + N_{A''}) = N_{B'}/(\Sigma N_B + \Sigma N_A)$$

and since the number of equivalents of any ion transferred will be proportional to its mobility and concentration,

$$N = k.UC$$

and

$$T_{B'} = U_B C_{B'}/(\Sigma U_B C_B + \Sigma U_A C_A)$$

For a binary salt this reduces to

$$T_B = U_B/(U_B + U_A)$$

but $\lambda_\infty = U_B + U_A$, where λ_∞ is the conductivity at infinite dilution, and further, the mobility is related to the absolute velocity of the ions under unit potential gradient (1 volt per centimetre) by the expression $U_B = F.u_B$, where F is 96,540 coulombs. Thus for potassium chloride at 18° $T_B = 0.497$ and $\lambda_\infty = 130.1$; hence $U_B = 0.497 \times 130.1 = 64.67$, and $u_B = 64.67/96,540 = 6.7 \times 10^{-4}$ cm. per second per volt per centimetre.

Apparatus and Method Employed. A simple form of apparatus with which the transport numbers of the silver and nitrate ions can be determined is shown in Fig. 1 (XI *). An N/10 solution of silver nitrate is prepared and 20 ml. of this are taken and weighed and the silver is determined volumetrically by means of ammonium thiocyanate. A saturated solution of copper nitrate is also made and is slightly acidified with nitric acid. About 8 ml. of the copper nitrate solution are placed in the tube B. Silver nitrate solution is then floated on top of the copper nitrate in B by filling a pipette and placing its tip in contact with the side of B just above the liquid surface and allowing the liquid to flow slowly out while at the same time gradually raising the pipette. When B has been filled up to the line of the cross-arm A and C are also filled with the silver nitrate solution.

The electrodes F and G are next inserted, F consisting of a silver wire cemented into a glass tube and G of a copper wire fixed in a similar manner. The cell is then connected in series with a milliameter, a voltameter, a

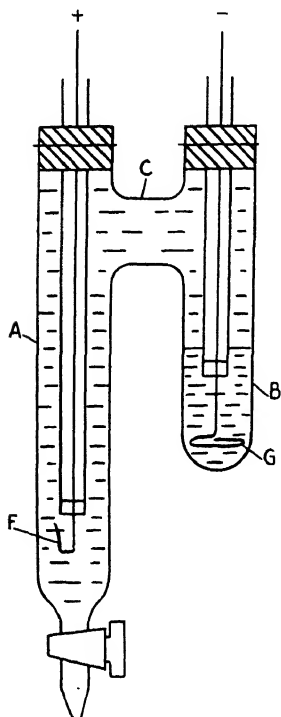rheostat and a contact key. An E.M.F. of from 50 to 60 volts is required which may be obtained from a battery of accumulators or from a direct-current lighting circuit if available. The current is cut down by means of the rheostat to 10 milliamps. For the present purpose a copper sulphate voltameter is sufficient. The solution is made by dissolving 15 grams of pure $CuSO_4 . 5H_2O$ crystals in 100 ml. of water and adding 5 ml. of concentrated sulphuric acid and 5 ml. of ethyl alcohol. A slow current of washed carbon dioxide is bubbled through the solution in the voltameter during the course of the experiment. The cathode is cleaned by dipping in dilute nitric acid, washing in distilled water and then in absolute alcohol, and is dried in the hot gases above the Bunsen flame. The cathode of the voltameter and the silver anode F are weighed. The apparatus is connected up and the current passed for 2 or 3 hours. The current is then stopped and the solution in the arm A is run off, very slowly to avoid mixing, into two weighed flasks, two-thirds into one flask and the remaining one-third into the other, and the weights of these two solutions are found. The weight of silver in each solution is determined volumetrically. The concentration of the second portion should be the same as that of the original solution, thus indicating that the experiment has not been carried on too long and that diffusion has not taken place into this section. The cathode of the voltameter is then washed, dried and weighed, as is also the anode F.

FIG. 1 (XI *)

Calculation of Results : Ag^+ and NO_3' Transport Numbers. The gain in weight W of the cathode, divided by 31·8, gives the number of equivalents carried by the current, and from this we calculate that the mass of silver nitrate derived from silver dissolved from F is $\dfrac{W}{31·8} \times 170$. This can be checked by the loss in weight of F.

If no silver had been transported this weight of silver nitrate would be present in A in addition to that originally there. If the original solution contained m_1 grams of silver nitrate in 100 grams of solution, and the final weight in the anode liquid were m_2 grams of silver nitrate in m_3 grams of solution, the final solution contains m_2 grams of silver nitrate in $m_3 - m_2$ grams of water.

The original solution contained m_1 grams of silver nitrate in $100 - m_1$ grams of water, and therefore

$$\frac{m_1}{100 - m_1} \times (m_3 - m_2) \text{ grams in } m_3 - m_2 \text{ grams of water.}$$

The change in the solution is therefore a gain of

$$m_2 - \frac{m_1}{100 - m_1} \times (m_3 - m_2) \text{ grams of silver nitrate.}$$

Had no transport occurred the gain would have been $\dfrac{W \times 170}{31 \cdot 8}$, hence the amount of silver transported is

$$\left. \frac{\dfrac{W}{31 \cdot 8} \qquad \dfrac{m_1}{100 - m_1} \times (m_3 - m_2)}{170} \right) \text{ equivalents}$$

and

$$T_{Ag} = \frac{\dfrac{W}{31 \cdot 8} - \left(\dfrac{m_2 - \dfrac{m_1}{100 - m_1} \times (m_3 - m_2)}{170} \right)}{\dfrac{W}{31 \cdot 8}}$$

and $T_{NO_3} = 1 - T_{Ag}$.

K^+ and Cl' Transport Numbers. The same apparatus can be used for the determination of the transport numbers of the potassium and chloride ions. An anode of potassium is obviously impossible; the silver anode is therefore replaced by one of cadmium cleaned with dilute nitric acid and amalgamated by dipping into mercurous nitrate solution, washing and drying. The arm B is filled first with 8 ml. of copper nitrate solution and then with N/2 KCl, as is the rest of the apparatus. A current of 10 milliamps. for 2 or 3 hours is used, and at the end of the experiment the solutions are titrated with N/2 silver nitrate solution. The transport number of the chloride ion is now the gain in equivalents of chloride ion in the anode compartment divided by the equivalents of copper deposited in the voltameter.

Findlay's Modified Apparatus. With the apparatus shown in Fig. 2 (XI *) a better separation of the middle portion is obtainable, since at the end of the experiment the clips HH can be closed and the solutions in A and B be removed without any possibility of mixing. In cases where a gas is evolved at the cathode, the tube B (Fig. 2 (XI *)) is replaced by B (Fig. 3 (XI *)), mercury or platinum being used as cathode.

Noyes' Apparatus. Noyes points out that the chief difficulty in the case of salts for which electrodes of the same metal cannot be used arises from the fact that free acid and alkali are generated at the cathode and anode respectively, and the hydrogen and hydroxyl ions produced rapidly pass into the middle portion of the solution owing to their high rates of migration. The use of the cadmium electrode as anode has been described above, but there is no corresponding way of preventing the dispersion of the hydroxyl ions produced at the cathode. The effect is that electrolysis can only be allowed to proceed for a short time with correspondingly small changes in the concentration of the solution. Noyes therefore used the device of adding alkali and acid to neutralize the acid and alkali formed. The apparatus consists of the two large U-tubes 3·5 cm. in diameter and joined by rubber tubing shown in Fig. 4 (XI *). The apparatus was filled
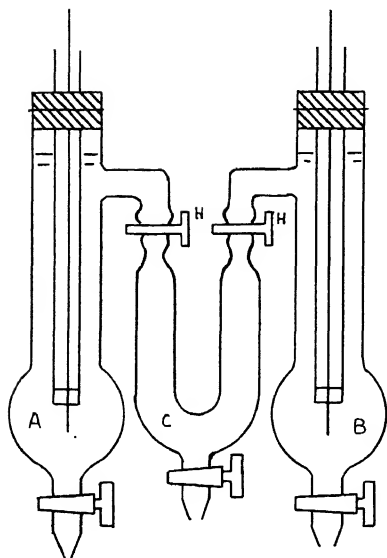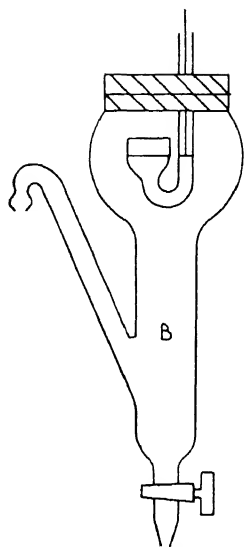
FIG. 2 (XI*)

FIG. 3 (XI*)

with solution, so that the arms E and F were full and the solution came about 2 cm. above the bend in the arms A and B, stoppers being placed 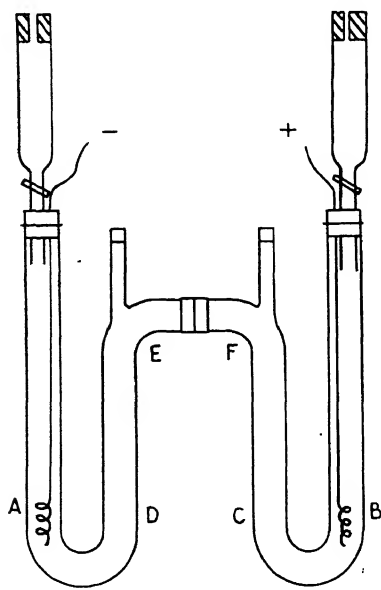in the small tubes of E and F. A few drops (a known weight) of phenolphthalein were placed in the bottom bend of each U-tube. The electrodes were of platinum wire and were raised during an experiment, so that the spiral was always only just below the surface. The dropping funnels were filled with N/2 or N/10 solutions of the acid and alkali corresponding to the salt in E and F, and were weighed before and after the experiment. The apparatus was kept in a thermostat, and after temperature equilibrium had been attained 2·5 ml. of acid solution was added at the cathode and 10 to 15 ml. of alkali at the anode. The electrodes were then connected through a switch, one 16 c.p. lamp, a Weston milliameter and a silver voltameter with a 110-volt D.C. circuit. The silver voltameter consisted of a platinum dish (as cathode) containing a 15 per cent silver nitrate solution. The anode was a silver plate wrapped in filter paper and supported just below the surface of the liquid. As the experiment proceeded, each time the pink colour appeared at the cathode 2·5 ml. of acid and

FIG. 4 (XI*)

alkali were added. At the end of 3 hours the current was stopped and the dropping funnels were removed and weighed, thus giving the amounts of acid and alkali added. Stoppers were placed in the arms A and B, and those in E and F removed. Three portions of the solution were withdrawn by means of a pipette for analysis, namely, those between E and F, D and E, and F and C. The U-tubes were now removed from the thermostat, a known quantity of acid was added to the anode portion to make its reaction acid and so prevent absorption of carbon dioxide. The two halves were separated, dried outside and weighed ; their contents were then transferred to two small flasks and the dried tubes were weighed alone.

Examples of Results. The five samples thus obtained were then analysed. An example of the results obtained is given :

BARIUM NITRATE, 0·1 MOLAL

Portion	Weight of portion	Salt content	Acid or base soln. added	Original salt content	Difference in salt content			Transport number
K	244·30	5·2507	40·53	4·2970	+ 0·9537	1·9334	Silver in voltameter	45·54
M1	180·57	3·8058		3·8070	− 0·0012	Time		
M2	199·75	4·2106		4·2112	− 0·0006	165 minutes		
M3	239·02	5.0368		5·0388	− 0·0020	Current		
A	205·23	(2·5491)		3·5000	− 0·9509	0·175 amperes		45·56
		(2·2196)	39·325					

Method of Steele and Denison. Steele and Denison used the apparatus shown in Fig. 5 (XI *) to determine the transport number in very dilute
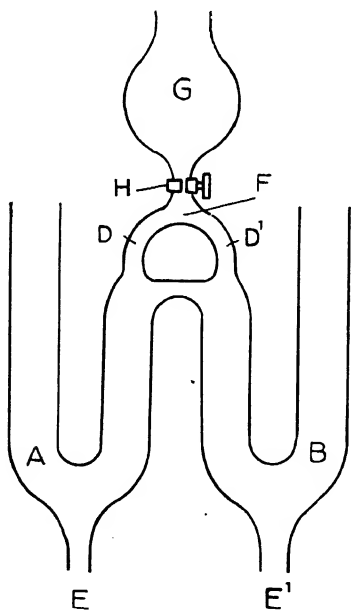

FIG. 5 (XI *)

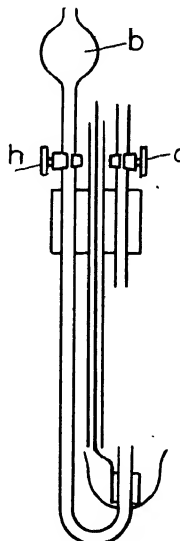FIG. 6 (XI *)

solutions. In using this apparatus the stoppers and electrodes shown in Fig. 6 (XI *) were inserted and the apparatus placed in the thermostat,

the tubes E, E′ being connected to rubber tubes and brought over the sides of the latter and there fitted with stopcocks. The solution to be examined was placed in G and, all stopcocks with the exception of H being closed, the inner arms of the two U-tubes were completely filled with solution, suction being used if necessary to remove air bubbles from F.

By opening one stopcock d the solution was allowed to rise to about 2 cm. above the electrode in A, and then similarly in B. Acid and alkali were added as in Noyes' method, but not in such large amounts. N/2 solutions of acid and alkali were contained in 30 ml. weighing pipettes, and where it was necessary to find the amount added these were weighed before and after an experiment. About 1 ml. of acid with a little indicator was put into b and by opening d and h was allowed to flow into the cup surrounding the electrode, where, owing to its greater density, it fell to the bottom of the cup. The quantity of electricity was measured with a silver voltameter and an E.M.F. of 60 volts was used. At the end of each period of twenty minutes the solutions were removed from the inner arms of the U-tubes. All stopcocks except H were closed, and then that attached to E was opened, whereby the solution in D ran out into a flask. E′ was then opened and the solution from D′ was received in another flask. Fresh solution was added through G. By this means experiments were possible for periods of 36 hours without mixing of the liquids from the two electrodes, thus enabling measurements to be made with very dilute solutions and small currents. In a modification capillary tubes attached to E and E′ allowed the solutions to run through the apparatus continuously.

Velocity of Hydrogen Ions : Lodge's Method. Lodge made a direct determination of the velocity of the hydrogen ion. He used a solution of sodium chloride in solid agar jelly. This solution was made just alkaline to phenolphthalein with caustic soda, so as to show the red colour of the indicator, and was contained in a horizontal tube fitted to two vessels containing dilute sulphuric acid and platinum electrodes. A current was then passed from one vessel to the other through the tube. As the hydrogen ions travelled along the tube they discharged the colour of the phenolphthalein and so enabled the velocity to be measured directly. Lodge obtained 0·0029, 0·0026 and 0·0024 cm. per second under a potential gradient of 1 volt per centimetre, while Kohlrausch's value is 0·0032 for the dilution corresponding to maximum conductivity. Lodge does not mention the concentration of his solution, probably it was sufficiently high to reduce the velocity; in addition, with this method it is improbable that the potential gradient is uniform along the tube owing to changes in the composition of the solution as the experiment proceeds.

Lodge's experiment may be repeated in the following way. A tube of uniform bore and about 40 cm. long and 1·5 cm. in diameter is taken and fitted by means of corks at each end to a wider tube bent up at a right angle. The agar jelly is prepared by taking about 16 grams of dry agar-agar and soaking it in 5 per cent acetic acid until it has completely swelled. It is then shaken three times with distilled water and allowed to stand for half an hour with distilled water, changing the water once. The excess of water is squeezed out and a solution of 5 grams of pure sodium chloride in 250 ml. of water is added. The mixture is heated on the water-bath to complete

solution, after which two or three drops of phenolphthalein are added and then caustic soda solution drop by drop until a well-marked red colour is developed. While still liquid the solution is poured into the tube and allowed to solidify there. The end-pieces are fixed on and N/2 sulphuric acid placed therein. The electrodes are held in position by corks having holes bored through them to allow the electrolytic gases to escape. The apparatus is now immersed in cold water and connected in series to about twenty-five storage cells and a rheostat. A voltmeter is connected in parallel with the tube containing the jelly. The rheostat is adjusted so that the voltage across the ends of the tube is numerically equal to the length of the tube in centimetres, thus giving a potential gradient of 1 volt per centimetre. After the boundary has moved far enough along the tube to enable its position to be marked, stop the current and mark the boundary by means of a piece of gummed paper. Allow the current to flow for an hour or more and again stop it. Note the time and mark the new position of the boundary. The velocity of the hydrogen ion can then be calculated in centimetres per second for a potential gradient of 1 volt per centimetre.

Whetham's Method. Whetham used the colour-boundary method without the use of jelly, using the apparatus shown in Fig. 7 (XI *). Two solutions having one ion in common, of equivalent concentrations, different densities, different colours, and nearly equal specific resistances, were placed one over the other in a glass tube. For example, in one case N/10 potassium carbonate and N/10 potassium bichromate were used. The denser solution is placed in the right-hand tube and the lighter in the left so that the boundary comes in the vertical connecting tube. On passing a current by means of the platinum electrodes the carbonate and bichromate ions travel in one direction and the potassium ions in the other, so that the boundary moves and its movement can be followed. The direction of the current must be such that the slower carbonate ion follows the quicker bichromate ion, in order to maintain a sharp boundary, for if the current flows from the liquid of high resistance to the one of low resistance, and one of the slower ions (necessarily from the high resistance solution) chances to get in front of the boundary, it finds itself in a region of lower potential gradient and so slows down and drops back into line, while if one of the faster ions gets behind the boundary it is in a region of higher potential gradient and so is urged forward more strongly.

FIG. 7 (XI *)

Whetham also made measurements with alcoholic solutions of cobalt salts and showed that the velocity of ions in agar solutions is but slightly less than in aqueous solutions. He also pointed out that precipitation reactions could be used, as, for example, with jelly solutions of barium
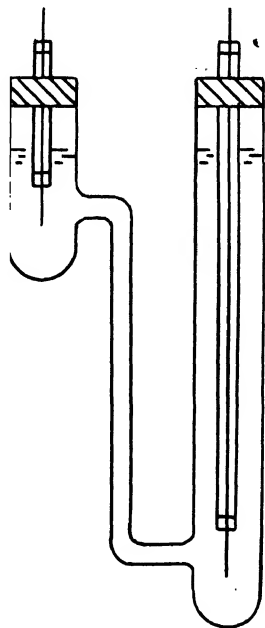
chloride and sodium chloride containing a trace of sodium sulphate, the movement of the barium ions being shown by the formation of a cloud of barium sulphate. Whetham calculated his potential gradients from the known conductivities of the two solutions, the area of cross-section of the tube and the measured value of the current used.

Masson's Method. Orme Masson obtained more accurate results by utilizing the fact that when a current passes from a solution of high to a solution of low resistance, the potential gradients are adjusted, so that the velocity of the slower ion in the region of high potential gradient is equal to that of the faster ion in the region of low potential gradient. A jelly solution of a colourless salt, for example potassium chloride, is placed in a horizontal tube 40 cm. long. End vessels containing the electrodes are fitted on and are filled with jelly solutions of potassium chromate and copper sulphate respectively. If the current is passed from the copper sulphate solution, through the potassium chloride to the chromate the slower copper ion follows the faster potassium ion in one direction and the slower chromate ion the faster chloride ion in the other. Stable and coloured boundaries are thus obtained and their movements can be followed. The potential gradient throughout the potassium chloride is constant and its value is obtainable from the conductivity and the current strength, so that the velocities of the potassium and the chloride ion are obtained under the same potential gradient.

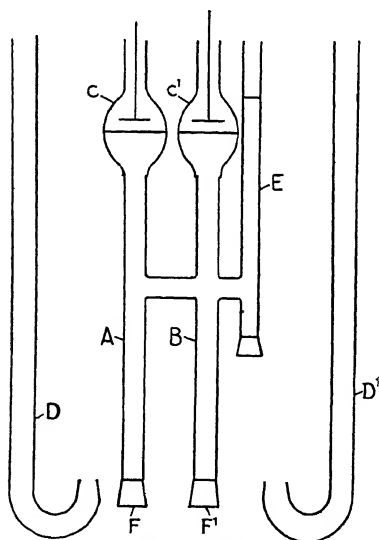**Steele's Extension of Masson's Method.** B. D. Steele has extended Masson's method by the discovery that under certain conditions of concentration and potential gradient the boundary between two colourless solutions can be followed by means of the difference in refractive index. The apparatus is shown in Fig. 8 (XI *), where the vertical tubes are about 1 cm. in diameter, the horizontal tube being somewhat larger. The ends of A and B are ground to fit C, C' or D, D' at their upper or lower ends. The stoppers F, F' are inserted and the solution is poured into E till the tubes A and B are full. The lower halves of C and C' are filled to a height of 2·5 cm. with 12 per cent jelly containing the substances which are to act as indicators in solution slightly more concentrated in equivalents than the solutions to be measured, and these bulbs are now placed on the ends of A and B and solutions of the indicators added above the jellies. The electrodes are made of metals which will give no evolution of gas. If the indicator solutions have densities greater than those of the solutions under examination the tubes D, D' are used to contain the indicators instead of

FIG. 8 (XI *)

the bulbs C, C'. Solution is finally poured into E to a height sufficient to balance the hydrostatic pressures in AC and BC'. In one experiment the solution was potassium chloride, while the indicators were lithium chloride and sodium acetate. On passing a current the indicator ions pass through the jellies into A and B, and since the lithium ion is slower than the potassium, and the acetate ion slower than the chloride, sharp boundaries are obtained, the position of which is apparent from the difference in the refractive indices of the solutions. It will be observed that the boundaries are in the aqueous solution, the jellies only serving to prevent mixing while the apparatus is being fixed up. A galvanometer was used to measure the currents and the position of the boundaries was observed by means of a cathetometer through the plate-glass window of the thermostat. A small gas jet was placed behind each tube and this, when viewed through the telescope appears to be cut by a dark line at the boundary. Measurements are made from a reference mark etched on each tube.

Conditions for Satisfactory Results. Steele points out that certain conditions must be fulfilled in order to get satisfactory results : (1) the ions must not react chemically on the solutions to be examined ; (2) during the electrolysis the solutions must not give rise to new ions which will move faster than and overtake the measured ion ; (3) the indicator ions must have a specific velocity less than that of the ions to be measured ; (4) the indicator solution must have a specific resistance not much greater than that of the solution to be measured, and when possible it is better to place the indicator solution above the measured solution, because, owing to its greater resistance, more heat will be generated, tending to decrease the density of the solution. The correct voltage to be applied in order to get a good boundary must be determined by experiment. With good conductors a narrower tube may be used, thus decreasing the current and the heating effect. The method is of course only a comparative one and give values of U/(U + V) only, but knowing the conductivity of the solution and the diameter of the tubes the actual resistance can be calculated, and this, with the value of the current used, enabled Steele to make an approximate calculation of the potential gradient and so of the absolute velocities. The calculation involves the unproved assumption that the migration velocity does not change with the concentration. We know in many actual cases that it does change.

Transport Numbers and Transference Numbers. The Hittorf transport number must be distinguished from the ' true transference number '. In the first method described in this chapter the ratio of salt to water is determined at each electrode before and after electrolysis, and no allowance is made for transport of water due to alteration in density of the solutions caused by alteration of their composition or to the migration of water (cataphoresis) on the passage of a current possibly due to the hydration of the ions. When these allowances are made the true transference numbers are obtained.

Effect of Change in Composition. To illustrate the effect of change in composition we may take the example of a normal solution of sodium chloride with a cadmium anode and a lead peroxide cathode quoted by Lewis. Lithium chloride and sodium acetate were the indicator solutions used. When one faraday passes the changes in the anode section are :

Disappearance of 1 equiv. of cadmium metal. Vol. change, $-$ 6·5 ml.

Formation of 1 equiv. of $CdCl_2$ in soln. ,, ,, $+$ 12·0 ml.

Loss of N_c (Hittorf No.) equiv. of NaCl, $N_c = 0.37$.

Vol. change, 0.37×18.0 ml.

Total increase $= -6.5 + 12.0 - 0.37 \times 18.0 = -1.2$ ml.

This would be the volume change if the anode side of the apparatus were closed and the cathode side open. If the cathode side only were closed the volume changes would be :

1 equiv. of PbO_2 disappears. Vol. change $-$ 6·7 ml.

1 ,, ,, water ,, ,, ,, $-$ 9·0 ,,

1 ,, ,, NaOH formed ,, ,, $-$ 4·1 ,,

1 ,, ,, lead ,, ,, ,, $+$ 4·6 ,,

N_a equiv. of NaCl disappear. $(N_a = 0.63)$

Vol. change -0.63×18.0 ml.

Total increase $= 4.6 - 6.7 - 9.0 - 4.1 - 0.63 \times 18.0 = -26.6$ ml.

There would therefore be a considerable flow of water towards the cathode. In practice both tubes were left open, and if we assume the liquids to have nearly the same density, the volume change will be evenly distributed and will be the mean of 1·2 in one direction and 26·6 in the other, i.e. 12·7 towards the cathode. The relation between the Hittorf number N_a and Denison and Steele's true transference number $N_{a'}$ is $N_a = N_{a'} - vc$, where c is the equivalent concentration, and v is the volume change in litres. In the present instance $c = 1$ and $v = -0.013$ litre ; since Denison and Steele found

$N_a = 0.614$, the Hittorf transport number

$N_a = 0.614 - 1 \times (-0.013) = 0.627$.
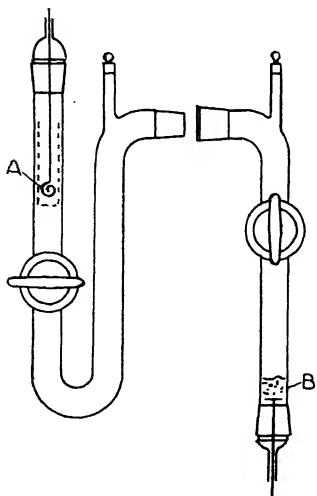
Washburn's Determinations. More reliable results would be

obtained if in the moving boundary method one of the sides were kept closed and the other open. To overcome the difficulty due to water transference caused by hydration of the ions, the suggestion was made by Nernst in 1900 that a small amount of some non-electrolyte which would not migrate with the current should be added. Water transference alone would alter the concentration of this substance and enable the amount of water so transferred to be estimated. The method was successfully applied by Washburn, using the modified form of Noyes' apparatus shown in Fig. 9 (XI *). The anode A consisted of silver wire surrounded by crystals of silver contained in an extraction thimble. The cathode B was a silver disc the surface of which is converted into silver chloride, and which is covered with

FIG. 9 (XI *)

a layer of silver chloride. These electrodes were found to be capable of carrying the necessary current for the period of the experiment without

the production of acid, alkali or gas. The apparatus was formed of tubing of uniform diameter throughout, including the bore of the stop-cocks. As reference substance raffinose (determined polarimetrically) was used. The quantity of electricity was determined by means of silver coulometers. Using the method with potassium chloride the following results were obtained :

	True transference numbers	Hittorf numbers
Potassium ion .	. 0·495	0·483
Chloride ion .	. 0·505	0·517

Determination of Transport Numbers by the Moving Boundary Method. A summary of all work up to 1910 is given by Noyes and Falk.[1] Recent work on this subject has been carried out by Longsworth.[2]

The theory underlying this method is discussed by Hartley and Moilliet [3] and MacInnes.[4]

The experimental details are described in Longworth's paper. The transference numbers of aqueous solutions of potassium chloride and other salts at 25° by the moving boundary method are determined, and the original should be consulted for details.

[1] *J. Amer. Chem. Soc.*, 1911, *33*, 1436.
[2] cf. *J. Amer. Chem. Soc.*, 1932, *54*, 2741.
[3] *Proc. Roy. Soc.*, 1933, A, *140*, 141, and *Trans. Far. Soc.*, 1934, *30*, 648.
[4] *J. Amer. Chem. Soc.*, *54*, 2758.

SECTION 2: CONDUCTIVITY OF ELECTROLYTES

Conductivity of Solutions. The methods of determining the conductivity of solutions most generally in use at the present day are those described in Kohlrausch and Holborn's *Leitvermogen der Elektrolyte*, which appeared in 1898. These methods give an accuracy of about 0·2 to 0·1 per cent. Within recent years very great improvements have been introduced by the work of Washburn, Taylor and Acree, Curtis and others, resulting in the possibility of making measurements 100 times as accurate as by the old methods.
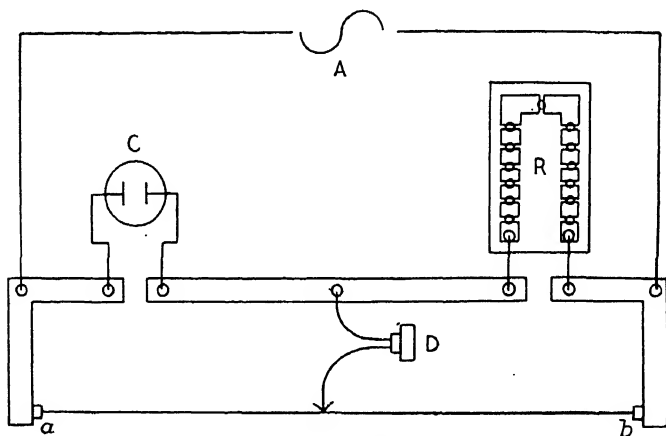

FIG. 10 (XI *)

The chief improvements introduced are: (1) The displacement of the induction coil by a high-frequency generator giving a pure sine wave form of a single frequency; (2) the use of telephone receivers tuned to resound to the frequency of the generator; (3) the use of resistance free from inductance and capacity; and (4) the proper use of electromagnetic shielding.

The electrolyte is contained in a cell with platinum electrodes, and the resistance of the cell is determined by the Wheatstone bridge method, as shown diagrammatically in Fig. 10 (XI *), where C represents the cell, R the resistance, A the source of current, D the detector, and *ab* the slide wire.

The Source of Current. A direct current cannot be used in the determination of the resistance of electrolytes because electrolysis would occur and the products set free at the electrodes would set up a back E.M.F. and alter the resistance of the cell, e.g. by interposing a layer of gas between the electrodes and the liquid; these effects are included in the term polarization. To avoid the polarization at the electrodes an alternating current is used, and to be effective for the purpose it should satisfy the following conditions:

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(1) The alternations should be sufficiently rapid and the quantity of electricity passing at each alternation should be small, so that no appreciable chemical change occurs ; (2) the quantity of electricity passing in one direction should be exactly equal to that passing in the other—if a small excess passes one way this will produce exactly the same electrode effects as a direct current of the same magnitude. In addition, the source of alternating current should give a wave of pure sine form. If this condition is not fulfilled and harmonics or overtones are present it is difficult to get a good minimum in the telephone ; e.g. Taylor and Acree [1] have shown that with platinized electrodes appreciable differences in the value of the apparent resistance may be produced by a change in the frequency of the measuring current, so that the point of balance for the fundamental frequency will not be the same as that for the overtones, with the result that a good sound minimum cannot be obtained.

Kohlrausch's Method. In the Kohlrausch method the induction coil was the source of current used. The best results were obtained with small coils having not many turns of wire, so that the total quantity of electricity passing at each pulse was small : the moving parts on these coils being small and light, a high note was obtained, to which the ordinary telephone and ear were more sensitive. It cannot be used when greater accuracy than 0·2 per cent is required, since the current departs very much from the ideal requirements. The deficiencies of the induction coil are well brought out by the oscillograms shown in Fig. 11 (XI*), A and B, both of which were obtained from small induction coils specially made for conductivity work. Such curves contain a number of harmonics and when the areas of the positive and negative loops are measured it is found that a considerable unidirectional current is present. Since the sum of the two currents in opposite directions is not zero, polarization must occur ; this was confirmed by

FIG. 11 (XI*)

Washburn by the inclusion of a silver coulometer in the circuit. Furthermore, there is no control over the frequency of the alternation, so that the advantage of using a tuned detector is lost.

High-frequency Generators. High-frequency generators have been specially designed to give a pure sine wave. The chief objections to them are that harmonics, especially the third harmonic, are not entirely absent ; the smaller forms are rather susceptible to small changes in the load or the exciting voltage ; a great deal of noise is unavoidable, so that the apparatus has to be placed at a distance from the measuring apparatus,
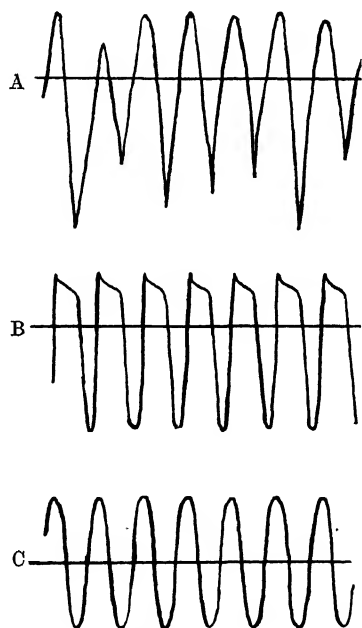
[1] *J. Amer. Chem. Soc.*, 1916, *38*, 2415.

and a considerable amount of auxiliary apparatus is required, so that the initial cost is very high. With proper attention and care a generator such as the Siemens-Halske will give very satisfactory results.

The Vreeland oscillator gives a sinusoidal wave free from harmonics, as shown in Fig. 11 (XI *) C. The simpler form is arranged to give frequencies of 1,000 or 500 cycles per second, while the larger form gives a frequency which can be varied between 160 and 4,200 cycles per second, and when set will remain constant to within 0·1 per cent for weeks and is not materially altered by the load varying. This apparatus has been improved by other apparatus and will not be described.

Detectors. Of the various methods that have been employed hitherto for detecting the point of balance, the two most important were the dynamometer and the telephone receiver. The Siemens electro-dynamometer when specially wound for low currents is not sufficiently sensitive when used in the ordinary way with the fixed and movable coils in series ; the sensitiveness is therefore improved by passing the main current from the source through the fixed coil, while the small current, produced by want of balance in the bridge, passes through the movable coil. Even then, however, the telephone is twenty times as sensitive, and this alone makes the dynamometer impossible for the most refined measurements. If it were not for this lack of sensitiveness most workers would prefer to use the galvanometer method instead of the telephone, over which it has several advantages. Thus it is only necessary to keep the current on a very short time in finding the point of balance, thus decreasing the chances of heating or of polarization ; the telephone is more of a strain on the worker, especially when measuring high resistance, and the sound is very faint. Absolute silence is not necessary, and there are the further advantages that the direction of the deflection gives at once the side of the bridge which has the larger resistance, and any creeping of the galvanometer after the point of balance has been found shows the presence of heating or polarization effects.

Telephone. The telephone receiver is at present the instrument which is capable of giving better results than any other. Washburn and Parker [1] calculate that for the extreme conditions represented by a temperature coefficient of resistance of 10^{-3} and temperature control to 10^{-4} (with a possible accuracy of 1 in 10 million), and a cell of ordinary dimensions, the audibility current for the telephone would require to be above 10^{-9} amps. Telephones of this degree of sensitiveness can be obtained, which is far greater than is required in ordinary work, where an accuracy of one part in one hundred thousand is the best that can be expected.

Wien has investigated the sensitivity of the ear for notes of different frequencies, and finds that the ear is most sensitive to notes having a frequency between 1,000 and 5,000 vibrations per second. A frequency of 1,000 cycles per second in the alternating current is the most satisfactory for general work, since it is within the limits of maximum sensitiveness of the ear, is not so slow as to allow of polarization effects, and is not so rapid as to increase unduly the reactance of the circuit. The telephone should have a natural period of resonance equal to that of the

[1] *J. Amer. Chem. Soc.*, 1917, **39**, 235.

source of current. When adjusted to great sensitiveness slight variations in the frequency may cause large variations in the sensitiveness. With many sources of power the third harmonic is present and is most troublesome in its effect, since it is impossible completely to balance it out. A great improvement is produced by tuning the receiver so as to correspond exactly to the fundamental, whereby the harmonic is very largely damped out. A telephone can be tuned to resound to a particular frequency by placing a small brass ring on top of the diaphragm and screwing down the cover so as to press the ring on to the diaphragm; the frequency will depend on the diameter of the hole in the ring, and the best value for this must be found by trial. Electrical tuning can be achieved by including in series with the telephone coils a capacity the value of which is found by experiment for any particular frequency. Tunable telephone receivers can be obtained from Messrs. Leeds and Northrup.

If a number of telephones are at hand it is very instructive to try several of them in finding the balance-point with a given arrangement of apparatus. While using the telephone absolute quiet is essential, so that any parts of the apparatus which are noisy should be placed at a distance or enclosed in such a manner as to reduce the noise as much as possible. Curtis advises the attachment of a stethoscope to the telephone receiver as a considerable aid to the comfort and accuracy of working, while a periodic interruption of the current in the telephone arm has also been recommended, since it is then easier to detect the balance-point. A very faint continuous buzzing may not be distinguishable from silence, but if the faint noise alternates with periods of silence the difference is readily noticed. The telephone should be insulated from the observer, e.g. if there is a metal head-band it should be covered with rubber. The leads to the bridge should be non-inductive and enclosed in a flexible metal sheath connected to earth as a protection against stray alternating electromagnetic fields.

Resistance. It has long been recognized that the resistance coils should be free from inductance and capacity. The high-resistance coils cause the largest errors, the effect of unbalanced capacity being to increase the uncertainty of the balance-point; e.g. under ideal conditions, if no sound is heard in the telephone when balance is tried at a point x on the slide-wire, a sound should be heard if the point of contact is shifted one-tenth of a scale division on either side. In practice, without using special apparatus and with high resistances, we can often move several scale divisions on either side of the balance-point without hearing any sound. This of course means that the balance-point itself is uncertain, and to avoid this uncertainty the whole of the bridge and its connexions should be as free from capacity and inductance as possible. Curtis and Grover [1] found that the errors due to inductance and capacity effects may be greater than 0·05 per cent when using 1,000-ohm coils of various makes. Washburn and Bell [2] prepared film resistances by sealing two platinum wires into a glass tube bent into a U-shape and connecting them by a thin film of platinum deposited on the glass. The film was obtained by using

[1] *Bull. Bureau of Standards (U.S.A.)*, 1912, **8**, 3.
[2] *J. Amer. Chem. Soc.*, 1913, **35**, 177.

a colloidal solution of platinum known as platinum-glanz, a fine pen being used to draw a line with this solution joining the two platinum wires. When the solution was dry the glass was heated to dull redness, whereby the platinum was embedded in the glass. These resistances gave very good results, the objection to them being that the temperature coefficient is 0·1 per cent per degree. An ordinary bifilar-wound 1,000-ohm coil may have an effective capacity of 0·0009 microfarad. Curtis has devised a coil which for the same resistance has an effective capacity of less than 1 micro-microfarad, that is, it is practically capacity-free. The use of this type of resistance coil may decrease the range of 'no sound' as much as twenty times. Taylor and Acree (loc. cit.) advise the use of Curtis coils wound on porcelain spools for all resistances greater than 10 ohms.

A resistance coil with a large capacity has a large power factor because of the poor dielectric which it contains, and because of the eddy currents induced in the inner layers of the coil. This causes the effective resistance with an alternating current to differ from the direct-current resistance, and also to vary with the frequency of the alternating current. In assembling the Curtis coils in box form care must be taken to keep them far enough apart to avoid the introduction of capacity. The dial decade type, with five dials and 1, 10, 100, 1,000, and 10,000 ohm units, is very convenient, since it gives all resistances from 1 to 100,000, and there is little chance of making an error in reading off the resistance.

The Measuring Bridge. The conductivity cell, when used with a high-frequency current and platinized electrodes so that polarization effects may be considered to be absent, may be thought of as acting as a resistance shunted with a capacity. The resistance box in the opposite arm of the bridge should be free from capacity and inductance, and must therefore be shunted across its terminals with a condenser in order to bring the phase of the two currents in the two branches of the bridge into agreement. Paper condensers should not be used, since they are not free from a power factor which introduces errors. A variable air condenser with low lead and plate losses and with very high insulation resistance is required. If the insulation is hard rubber it should be protected from the action of light when not in
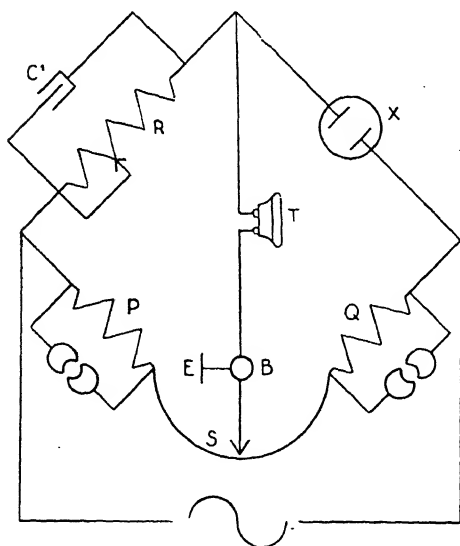

FIG. 12 (XI *)

use and should be kept clean and dry. With a slide-wire 1 metre long it is possible to read with ease to one-quarter of a millimetre, and if the point of balance is at the middle of the wire, as it always should be, this means

an accuracy of 1 part in 2,000. This degree of accuracy is insufficient, while to get an accuracy of 1 in 100,000 would require a wire 50 metres long. To overcome this difficulty Leeds and Northrup make a slide-wire about 470 cm. long wound on a marble drum 15 cm. in diameter, so that there are ten turns of wire having a resistance of about 27 ohms. The slide-wire is provided with extension coils at either end, each having a
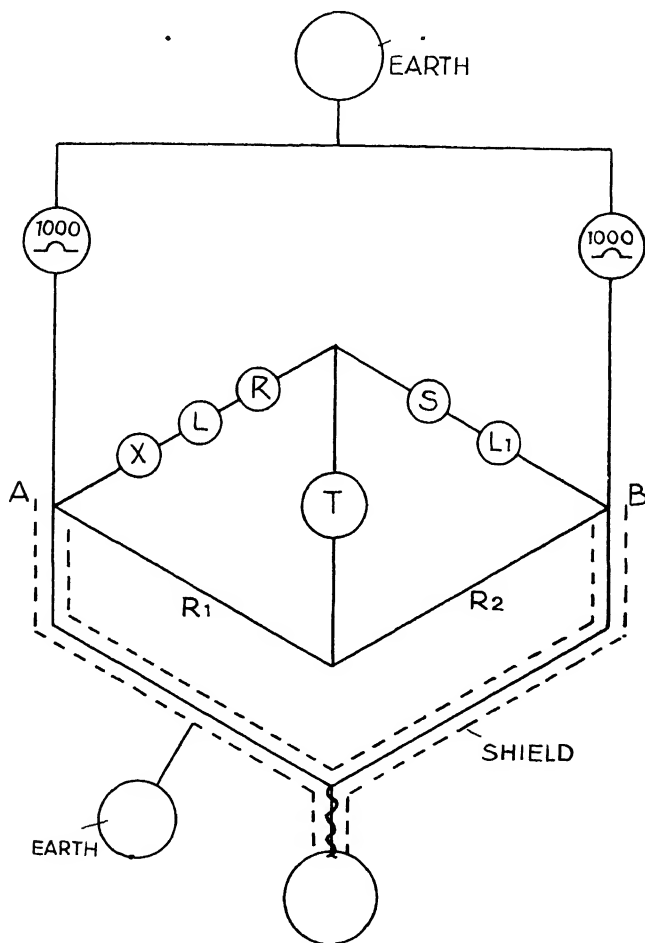

FIG. 13 (XI *)

resistance four and a half times that of the slide-wire and giving the same result as a slide-wire ten times as long and having a total resistance of 270 ohms. The end coils should be wound on the Curtis principle and can be short-circuited when necessary.

In connecting up the bridge twisted leads of the same form and length should be used on either side. Fig. 12 (XI *) shows the arrangement described by Washburn. Here S represents the slide-wire, P and Q are the extension coils with the short-circuiting plugs, and T is the telephone

receiver connected to the slide-wire contact-maker at the point B, which is also connected to earth. X represents the conductivity cell, the resistance of which is balanced against that of the Curtis coils R, and the terminals of the latter are shunted with the condenser C.

Taylor and Acree (*loc. cit.*) point out that the circular slide-wire may introduce very large errors owing to self-induction in the slide-wire and
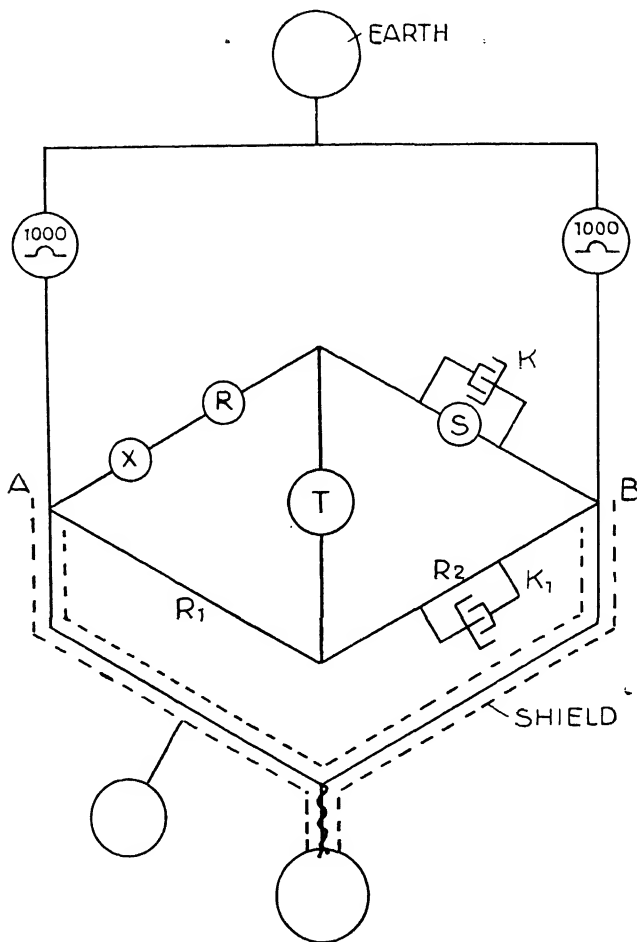

FIG. 14 (XI *)

to the capacity between the slide-wire and the metal cover. They describe two bridge methods in which the resistance is obtained by substitution; these methods are illustrated in Figs. 13 (XI *) and 14 (XI *). In the first figure the place of the slide-wire is taken by the two Curtis ratio coils, R_1 and R_2, which may be 100, 500, or 1,000 ohms. In the same arm as the electrolytic cell X is included a standard variable inductance L and a set of Curtis coils R, giving resistance from 0·001 to 10,000 ohms. The fourth arm contains a variable resistance S and a fixed inductance L_1,

having a value greater than the smallest value of L. The current from the Vreeland oscillator enters at A and B, the leads being enclosed in a metal cover connected to earth, while A and B are also earthed through high resistance as shown. In making a measurement the resistance of R is first set at zero with the cell in the circuit, and the resistance S and the inductance L are then adjusted until silence is obtained in the telephone. The cell X is then removed and the resistance R and the inductance L are then varied until silence is again obtained. The value of R then gives the resistance of the cell with its leads, and it is only necessary to keep the temperature of R regulated, since all the other resistances cut out when the two measurements are made at the same time. The second diagram shows an improved form of the Kohlrausch method adapted to allow of the measurement of the resistance by substitution. The letters have the same meaning as in the first figure, the inductances L and L_1 being replaced by the air condensers K and K_1. Balance is obtained as before with the cell in the circuit and R equal to zero by altering the value of S and K ; the cell is then removed and silence in the telephone is again obtained by altering R and K.

Bridge Design. Important improvements in the design of the alternating current bridge for the measurement of electrolytic conductivity have been introduced by Jones and Josephs.[1] The essential features of their method are (1) Generation of the A.C. current by means of a valve oscillator, (2) Increase in sensitivity by using an amplifier with the telephone, (3) Improvement in method of earthing the bridge, (4) Use of specially constructed resistance boxes in which di-electric losses are reduced to a minimum.

(1) *Source of A.C. Current.* The thermionic valve generator for supplying A.C. current to the bridge is shown in Fig. 15 (XI *). Such a source has several important advantages over the Vreeland oscillator (described in 2nd ed. of *Physico-Chemical Methods*, p. 696), which requires 5 amps. at 100 D.C. volts, and requires therefore either a large battery or motor generator to operate it. The
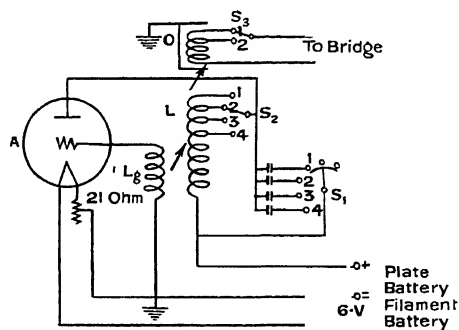

FIG. 15 (XI *)

oscillator has, furthermore, a low efficiency for such purposes, and when operated by a motor generator erratic external noises are produced. The valve generator is cheap to build, is easily adjustable in frequency and voltage, and produces a much smaller external magnetic field than the Vreeland oscillator. It possesses only one slight harmonic. This difficulty may be eliminated by accurate tuning of the telephone receiver.

(2) *Telephone Receiver.* The sensitivity of the bridge setting is considerably increased by using with the telephone a valve amplifier tuned to the note of the generator. Two stages of amplification are usually sufficient

[1] *J. Amer. Chem. Soc.,* 1928, 1049.

to give an accuracy of one part in a million, in the setting of the bridge. Amplification in this way allows the use of high resistance cells in which errors due to heating and polarization are minimized, and permits the design of a cell, as a long narrow tube, which gives better thermal contact with the liquid in the thermostat.
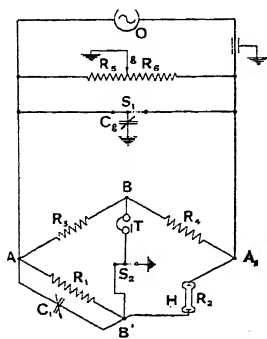

FIG. 16 (XI *)

(3) *Improved Method of Earthing*. In bridge experiments of this type considerable capacity exists between the telephone coils and the observer or between the primary and secondary of the transformer, if an amplifier is used. These defects may be eliminated by a special earthing device which is shown in Fig. 16 (XI *).

It is a modification of an earthing method originally due to Wagner. An auxiliary resistance $AR_5R_6A_1$ is placed in parallel with the bridge. It is provided with a sliding contact which is earth connected, and a variable air condenser Cg, one side of which is earthed, the other side being connected by a switch S, to A or A_1.

The resistances R_5 and R_6 are adjusted so that the ratio $\dfrac{R_5}{R_6}$ is approximately equal to $\dfrac{R_3}{R_4}$

The earth is adjusted as follows:

1. The bridge is approximately adjusted by altering R_1 and C_1.
2. By means of the switch S_2 the telephone is disconnected from B_1 and earth connected.
3. The sliding contact and condenser Cg are adjusted until no sound is heard in the telephone. B is then at earth potential.
4. The telephone is now again connected to B_1, by the switch S_2.
5. Final adjustment is made by varying R_1 and C_1. If this second adjustment is very much different from the original, the whole process is repeated.

(4) *Design of Special Resistance Boxes*. For high-precision work the ordinary resistance boxes available in the laboratory are unsuitable, since they have alternating current error in the upper ranges (i.e. for resistances above 1,000 ohms). Their effective resistance at high frequency is less than their value at low frequency, the percentage error increasing with the frequency, and the resistance of the box. The fact that the error is a negative one shows that it is not due to the 'skin effect', since this would lead to an increase in effective resistance at high frequencies. The error is attributed to dielectric losses in the insulation of the coils. This loss is approximately proportional to the resistance across which it is shunted, to the capacity, and to the frequency and power factor of the particular kind of substance within the electric field.

$$R = R_R(1 - R_R Cwn + \ldots)$$

where w is frequency, C the capacity and n the power factor.

The power factor is zero for air, so that resistance boxes should be constructed so as to bring the strong dielectric fields in air far apart.

The capacity is an important factor in the dielectric loss, and it is largely dependent on the dielectric constant of the insulator, so that a substance such as hard rubber of low dielectric constant should be used for insulation. Akin to this error caused by dielectric loss is the error caused by the dissipation of energy in appended coils, which are not in use. In the usual form of box, the coils which are not in use, although not in the circuit, are attached at one end to the coils which are in use. With A.C. current this permits the current to flow into the appended coils in sufficient amount to charge up the capacity between the coils, and the rest of the circuit. This charging current passes through the resistance of the coils, and dissipates energy in the form of heat, thus influencing the apparent resistance. The effect produced is equivalent to the introduction of an additional branch consisting of a small capacity and a high resistance in parallel with the coil in use, thereby diminishing its effective resistance. To avoid error due to this cause, the mutual capacity between the different parts of the resistance box should be kept low. This is accomplished by designing the box so that the coils, lead wires and terminals are as far apart as possible. The coils should in addition be wound non-inductively, and hysteresis and eddy current losses associated with any unavoidable inductance should be made as small as possible by avoiding entirely the use of iron, or masses of metal of any kind within the magnetic field.

Thin wires to avoid ' skin effects ' should be employed, and they should be composed of metals of low temperature coefficient (e.g. manganin or other similar wire).

Jones and Josephs have designed a high precision bridge in accordance with the above principles and for particulars of this the original paper [1] should be consulted.

Shedlovsky's Bridge. Shedlovsky [2] considers the theory of the disturbing capacity effects in an A.C. Wheatstone bridge and develops the basis for designing proper screening : some of the more important points in his screened bridge are :

1. *Balancing Condensers.* A twin (double) variable air condenser across the measuring resistance and the cell is used to balance out reactance at the cell due to polarization at the electrodes (a single variable condenser may have a zero residual capacity which is too large). One condenser has a capacity of $250\mu\mu$ F. and is easily constructed from the ' tandem type ' condenser of the General Radio Co. The other, connected in parallel, is similarly constructed from two microcondensers and has a maximum capacity of $10\mu\mu$ F. and a vernier control knob.

2. *Ratio Arms.* These are connected to the bridge by a double-pole double-throw reversal switch, S_r (Fig. 17 (XI *)) and by taking the mean of the readings with the ratio arms in the two positions correction is obtained for slight variations in the resistances and reactances of the two arms. The ratio coils are surrounded with symmetrical shields as shown by the broken lines and consist of two closely matched Ayrton-Perry coils of 1,000 ohms wound on flat bakelite cards. The flat coils are mounted

[1] *J. Amer. Chem. Soc.*, 1928, 1049. [2] *Ibid.*, 1930, *52*, 1793.

parallel to each other and symmetrically between three parallel copper
plates 3·8 cm. apart: the plates are soldered to a copper strip which joins
the two resistance coils.

3. *Detector*. A two-stage audio transformer coupled amplifier (Fig. 18
(XI *)) with sensitive telephones is used. The output from the bridge is
fed into the primary of the first transformer. By means of the switch
S^D (Fig. 18 (XI *)) the detector may be connected either for recording the
balance in the main bridge or for earthing adjustment.

4. *The Earthing Circuit*. This consists of two 1,000-ohm bifilar coils
(Leeds and Northrup) and a 10-ohm rheostat (Fig. 17 (XI *)) to the two
ratio arms extremities and to earth. In addition there is a variable air
condenser with a vernier control knob, connected between the earth E
and the point A or C as required. The various parts of the bridge, including
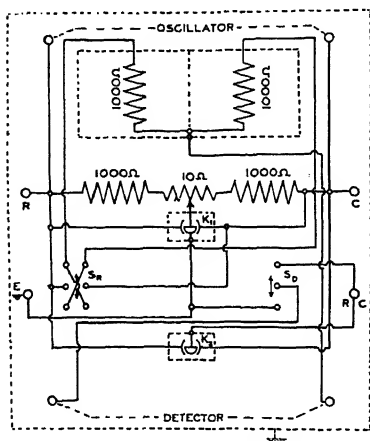the oscillator and detector, are shielded from external electrostatic disturb-

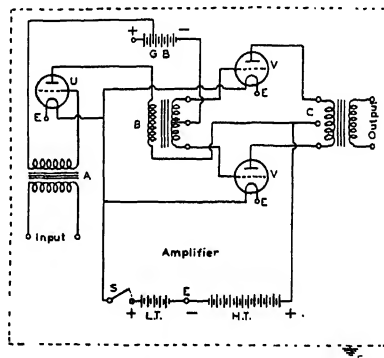FIG. 17 (XI *)
Bridge and Earthing Circuit

FIG. 18 (XI *)

ances by the earthed metal shields surrounding them, the various earth
points E all being brought together by soldered connexions.

The ratio arms, earth resistances, condensers, and the reversal and
detector switches (Federal anti-capacity) are all mounted in an earthed
copper screened box as shown diagrammatically in Fig. 17 (XI *). The
top of the box consists of a brass plate in which the terminals are mounted
with adequate insulation of transparent bakelite.

5. *Measuring Resistance*. The resistance standard consists of three
parts, a five-dial box of bifilar coils containing decades of 1/100, 1/10, 1,
10 and 100-ohm steps is mounted in a shielded box. The screening in the
box has a clearance of not less than 6·4 cm. from any of the coils or contacts
whereby the effect of the screen capacity on the resistance is negligible.
The control knobs for operating the resistance dials are on the outside of
the box on a brass plate which forms part of the shielding: they are fastened
to the dials through stout bakelite rods. The complete shielding of these
resistance dials as well as the condenser K is of great convenience in elimin-
ating 'hand effect' in measurement.

Temperature effect on the coils is not negligible when working to 0·01 ohm and it is not the same on every coil, it is therefore necessary to control the temperature of the 1,000 ohms step decade and the 10,000-ohm coils. These coils (Leeds and Northrup), which are of a woven type, forming one loop are practically reactance free, are compact and more constant in resistance than the card-wound type, being subject to very slight mechanical strains. The 1,000-ohm decade is mounted in air in a glass jar which is immersed in the metal-shielded, oil-filled thermostat which holds the conductivity cell and which is regulated to 0·005°. The 10,000-ohm coils are mounted separately in large test tubes which are sufficiently spaced in a wooden frame and immersed in the thermostat. The 1,000-ohm decade is permanently connected to the resistance box with a stiff heavy wire avoiding close screening. The necessary connexions in the thermostat of the cell and measuring resistances are made with short heavy strands of bare copper wire through mercury cups. To avoid appreciable 'dead end' effects, the 10,000-ohm coils are appended one at a time as needed. Connexions to the bridge box of the various units are made with flexible copper screened stranded wire, the screening being earthed.

FIG. 19 (XI *)

6. *Oscillator*. This (Fig. 19 (XI *)) is a double balanced oscillating circuit which gives alternating current of very good wave form and of more constant frequency and intensity than that generated by the usual type of one-tube oscillator. The frequency can be varied from 600 to 8,000 cycles by means of the four mica condensers A_1, A_2, A_3, and A_4, which can be thrown in parallel by means of the switch shown at S, the total capacity being $0·1\mu$ F. The valves used are UX201A, the condensers D have each a capacity of 1μ F. and the resistances R_1 and R_2 are of 0·01 megohm. The coil O has 100 turns and each of the coils C has an inductance of 50 millihenries. The voltage supplied can be varied by looser coupling of the 'pick up' coil. A calibrated vacuum thermocouple is joined in the output circuit to measure the current supplied to the bridge. H.T. is a high-tension battery of 90 volts and L.T. a low-tension battery of 6 volts. It is very important to use separate batteries for the oscillator and detector circuits. The oscillator should be at some distance from the bridge and is connected by duplex cable in flexible copper sheathing which is earthed. A switch near the bridge controls the filament current.

The dynatron (tetrode) oscillator shown in Fig. 24 (X *) has applications also in conductivity work and can be recommended.

Dowling's Method of Measuring Electrolytic Resistance. A method of measuring electrolytic resistance at radio frequencies is described by Dowling and Preston.[1] The method is an extension of the ultramicrometer circuit described by Dowling,[2] and consists in comparing the electrolytic resistances with wire resistances at a frequency of $0·46 \times 10^6$
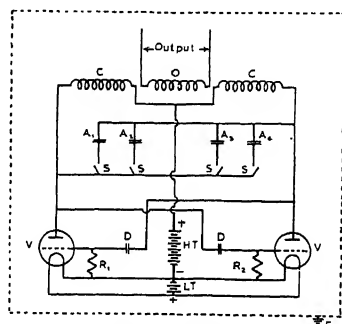
[1] *Phil. Mag.*, March, 1923.   [2] *Ibid.*, 1921.

cycles. It is extremely sensitive and the values obtained for the resistances are in excellent agreement with those obtained by the ordinary Kohlrausch bridge method. A similar principle has been used by Teegan,[1] who employs a Hartley oscillating circuit giving alternating current at a frequency of 1,000 cycles. He has compared the measurement made at low and radio frequencies, and finds that at radio frequencies approaching 10^6 cycles apparent increases are obtained in the electrolytic resistances, associated with capacity and electrode effects at these high frequencies. It would seem to follow from these results that very high frequency current is unsuitable for accurate measurement of electrolytic resistance.

Cenco-Stone Impedance Bridge. This bridge measures the impedance, or the resistance in alternating current circuits, whether arising from a resistance, inductance, or capacitance in terms of resistance, inductive reactance, or capacitance reactance, depending on the variable standards of impedance used to balance the unknown impedance, with a reproducibility of 1 part in 1,000 and an absolute accuracy of about 0·25 per cent.

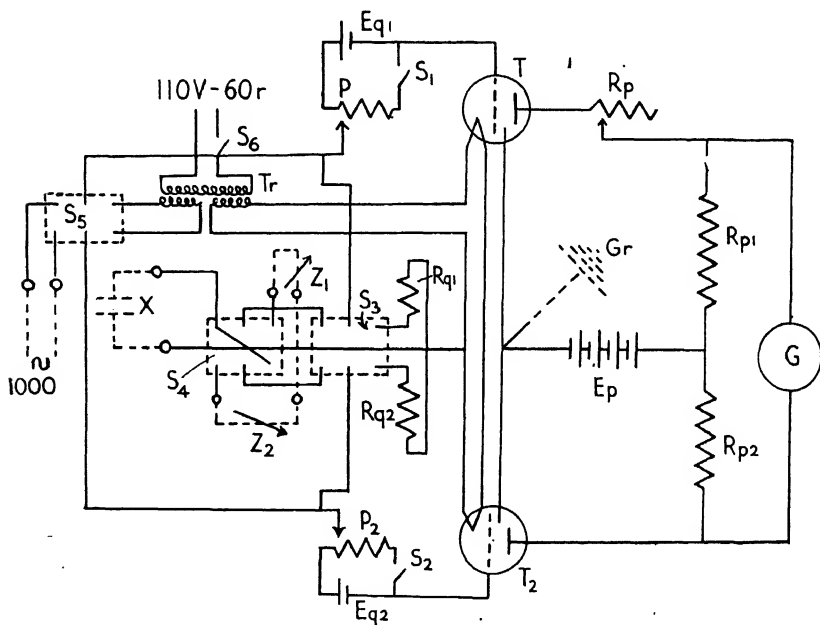The bridge is of particular use in the measurement of electrolytic con-

FIG. 20 (XI *)

ductivities because the capacity effect of the conductivity cells used is negligible.

The circuit employed is shown in Fig. 20 (XI *) and employs two thermionic tubes, the plate currents of which are balanced visually by a very sensitive null point galvanometer through the adjustment of grid potentials derived from small batteries and the superimposed alternating current used in the impedance measurement. After the plate currents are balanced,

the actual measurement of the impedance of the unknown is made by introducing the unknown and a standard of impedance into the grid circuits of the two thermionic tubes and re-establishing the balance by adjustment of the standard. A second measurement is then made by switching the unknown to the grid circuit of the other tube and introducing a second impedance standard in the grid circuit of the tube formerly in series with the unknown. Balance is established by adjustment of the second impedance standard. The value of the unknown impedance X is given by the formula

$$X = \sqrt{Z_1 . Z_2}$$

Measurement of Electrolytic Conductivity. Here standard resistance boxes are used for the impedances Z_1 and Z_2. The procedure may be divided into two separate operations, the first, the balancing of the two thermionic tubes to their proper cut-off potentials and, the second, the balancing of the unknown impedance against the standard impedances. Fig. 20 (XI *) shows that portion of the diagram of the circuit employed in balancing the thermionic tubes at their cut-off potentials. The diagram is seen to resemble the Wheatstone bridge in some respects.

(1) The knobs P_1 and P_2 controlling the steady D.C. potential applied to the grids of the tubes T_1 and T_2, are turned to their extreme counter-clockwise position whenever the instrument is not in use. In this position the switches S_1 and S_2 are open, and if the circuit is accidentally closed through contact of other switches in the circuit, the maximum negative potential is lower than the cut-off potential of the tubes. When the filaments are lighted, no current flows in the plate circuit and so the galvanometer G is protected from violent deflections.

(2) Close switch S_3 to place the fixed resistances R_{g1} and R_{g2} in the grid circuits of the tubes T_1 and T_2.

(3) Close switch S_6, which furnishes 110-volt, 60-cycle A.C. to the transformer Tr, from which the proper voltage is supplied to the filaments of the tubes T_1 and T_2.

(4) Turn knob R_p to the extreme counter-clockwise position : this is later used to compensate for the inequality of the tubes.

(5) Turn the potentiometer knob P_1 clockwise till the galvanometer G just shows a tendency to deflect. Turn potentiometer knob P_2 clockwise until the galvanometer just shows a tendency to deflect in the opposite direction. The tubes T_1 and T_2 are now operating at their 'cut-off' potentials and no current flows in the plate circuit of either tube. Switches S_1 and S_2 are part of the potentiometers and are closed when the knobs P_1 and P_2 are slightly moved from their extreme counter-clockwise positions.

(6) Close switch S_5 to apply the A.C. of the frequency to be applied to the grids of the tubes T_1 and T_2.

(7) Operation 6 will ordinarily produce a deflection of the galvanometer G, because the characteristics of the tubes T_1 and T_2 in general are different. This difference is compensated by turning knob R_p clockwise and thus introducing resistance in the plate circuit of the tube T_1. The plate current will be lowered until it becomes equal to the plate current of tube T_2 as indicated by zero deflection of the galvanometer. If the deflection is not

restored to zero by this manipulation, undo all the operations in their order
to the beginning of the procedure, interchange the tubes T_1 and T_2 and
repeat all operations to this point. It will now be possible, by manipula-
tion of knob R_p, to produce a zero deflection of the galvanometer. The
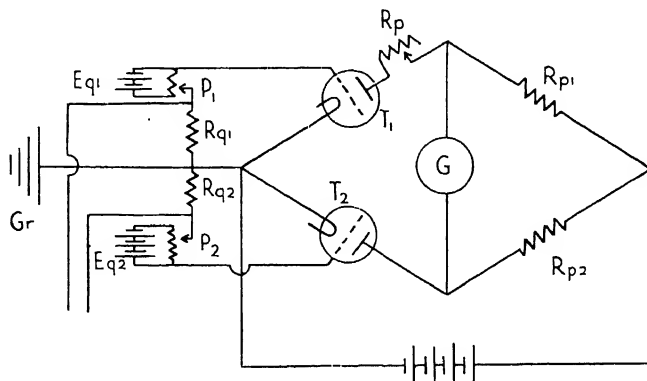bridge is now ready for making the measurements.

FIG. 21 (XI *)

Measurement of the Unknown Resistance. Switch S_3 is changed to the
position marked S–Z so as to replace the fixed resistances R_{g1} and R_{g2} by
the unknown resistance X and the variable standards of resistance Z_1 and
Z_2. The circuit of Fig. 21 (XI *) is thus changed to Fig. 22 (XI *).

(2) Close switch S_4 on the Z_1 position, so placing the unknown resist-

FIG. 22 (XI *)

ance X in the grid circuit of tube T_2 and the second variable standard of
resistance Z_1 in the grid circuit of tube T_1.

(3) Adjust the resistance Z_1 to bring the galvanometer to zero.

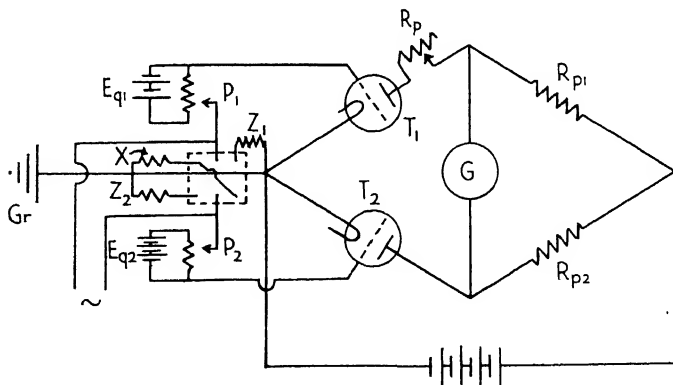(4) Close switch S_4 in the Z_2 position : this places the unknown resist-
ance X in the grid circuit of tube T_1 and the second variable standard of
resistance Z_2 in the grid circuit of the tube T_2.

(5) Adjust the resistance Z_2 to bring the galvanometer back to zero.

(6) By rocking switch S_4 back and forth, adjust Z_1 and Z_2 until a permanent balance is established in either direction as is indicated by no deflection in the galvanometer in either position.

(7) Calculate X from the values of Z_1 and Z_2 from the formula

$$X = \sqrt{Z_1 . Z_2}.$$

In this method the capacity of the cell is negligible : thus in the case of a cell with electrodes having an area of 1 sq. cm. and placed 1 cm. apart, if the resistance of the cell is 10^6 ohms and an A.C. of 1,000 cycles frequency is used, calculation shows that

$$R = X\sqrt{(1 + 0.309 \times 10^{-6}.K^2)}$$

where X is the measured impedance and K is the dielectric constant. The bridge has a range from a few ohms up to several megohms.

In measuring capacitances, using variable standard condensers, values as small as 500 micro-microfarads may be measured.

Measurements on inductances may be made as low as 10 millihenries.

The Thermostat in Conductivity Work. For accurate conductivity work the temperature of the solution must be kept constant to about $0.005°$ (see e.g. Thyratron relay-Thermostats, Chap. VI, S. 1) since electrolytes have, on the average, a coefficient of 2 per cent per degree. To accomplish this and at the same time to have regard for certain electrical precautions, a thermostat was constructed by D. Belcher, who supplied the following note.

The container was a copper tank $24 \times 20 \times 18$ inches deep. It was encased in a wooden box, and between copper and wood there was about 2 inches of mineral wool. As Jones and Josephs [1] have pointed out, appreciable errors may result from the use of water in a thermostat in alternating current measurements, the tank was filled with mineral colza oil. Stirring was accomplished by a vertical propeller driven by a $\frac{1}{72}$-h.p. D.C. motor which was operated at a speed considerably less than its rated 934 r.p.m. The efficiency of stirring is shown by the fact that no variations of more than $0.001°$ could be detected when a Beckmann thermometer was moved about in the thermostat.

The heating was done with a coil of thin nichrome wire wound spirally on an ebonite frame. The size of the wire and its spacing was such that the thermal lag was negligible. The thermal regulation was attained with the apparatus shown diagrammatically in Fig. 5 (VI) in ' Thermostats ', Vol. I, p. 190. The regulator H consisted of a steel tube some 12 inches long which contained about 400 ml. of carefully cleaned mercury. At C the glass capillary was sealed in with De Khotinsky cement and in this was set the regulating needle, which was of steel. Contact of the needle with the mercury applies a stopping potential from the battery B through the $\frac{1}{4}$ megohm resistance R_1 to the grid G of the thyratron valve T. When the contact is broken a plus potential is applied to the grid through the 1 megohm resistance R, R_1 and R_2 serve to protect the battery and regulator from excessive current. The anode circuit is supplied with 200-volt 50-cycle current from the A.C. mains. The anode current passes through a

[1] *J. Amer. Chem. Soc.*, 1928, *50*, 1049.

0·5 amp. fuse to protect the thyratron from overload, and through the nichrome heating coil M. Since the thyratron can be severely injured by applying potential to the anode before the filament is fully heated the switch S is not closed until some 15 seconds after the mains power has been applied. For the same reason the mains current passes through a magnetic switch which cuts out the power if for any reason there is a momentary interruption. The particular thyratron used was B.T.1 made by the British Thomson-Houston Company. Its mean anode current is 0·3 amp, but since there is half-wave rectification the power output is considerably less than 30 watts. The advantages of the thyratron for thermostatic control are obvious. It has no mechanical parts which can stick in the manner of mechanical relays and the minute grid current ensures that there will be no fouling of the mercury contact. The thermostat could be relied upon to within $\pm$ 0·001° and functioned with no serious trouble for over two years.

Conductivity Cells. The question of the design of cells for conductivity work has been considered in detail by Washburn.[1] He showed that the cross-sectional area between the electrodes must not be less than a certain minimum value which is fixed by the time to make the bridge setting, the specific conductivity which it is desired to include within the range of the cell and the percentage accuracy desired.

Assuming the values shown below for the quantities involved, he has designed four cells to cover the range of conductivities from 1 to $1·6 \times 10^{-7}$ reciprocal ohms. The conditions assumed were : Resistance of slide-wire, 250 ohms ; resistance of telephone, 150 ohms ; audibility current, 2×10^{-9} amps. ; time required for a setting, 10 seconds ; minimum resistance of cell, 100 ohms ; maximum resistance of a cell, 10^4 ohms ; temperature coefficient of resistance of ordinary electrolytes, 0·02 ; and for conductivity water, 0·05 ; and heating effect of the current not to exceed 0·0005°.

The cells, which are of the pipette form to facilitate filling, are shown in Figs. 23 (XI *), 24A (XI *) and 24B (XI *). For conductivities less than $1·6 \times 10^{-7}$ he recommends a cell having electrodes consisting of coaxial cylinders 4 cm. long and 4 cm. across, the cylinders being 3 mm. apart. For conductivities between the range $1·6 \times 10^{-7}$ and 10^{-5}, i.e. suitable for conductivity water of the greatest degree of purity which is stable in the presence of air, the cell shown in Fig. 23 (XI *) is suitable ; the electrodes are not platinized, but are roughened by sand-blasting and consist of two discs 4 cm. in diameter and 2 mm. apart. Also like Fig. 23 (XI *) is the cell for the range 10^{-5} to 10^{-4} reciprocal ohms, but the electrodes are lightly platinized and are of the same size as the last, but are 3 mm. apart. The cell for the range 10^{-4} to 10^{-2} is shown in Fig. 24A (XI *). Here the electrodes are well platinized and consist of horizontal discs 1·5 cm. in diameter and 1·8 cm. apart, while for the most concentrated solutions the cell shown in Fig. 24B (XI *), having a range from 10^{-2} to 1 reciprocal ohms and having heavily platinized electrodes of convex form is used. The cell is narrowed down to a diameter of 0·36 cm. between the electrodes, which are 10·1 cm. apart. Besides these cells many other forms are in use, more especially those of Ostwald and of Kohlrausch, figures of which may be

[1] *J. Amer. Chem, Soc.,* 1916, **38**, 2431.

found in any catalogue. A form of cell that is useful for many purposes has a pipette form and is open at the bottom so that the conductivity of the contents of a beaker, for example, can be determined by placing the cell in the liquid. The electrodes should be of the purest platinum, free from
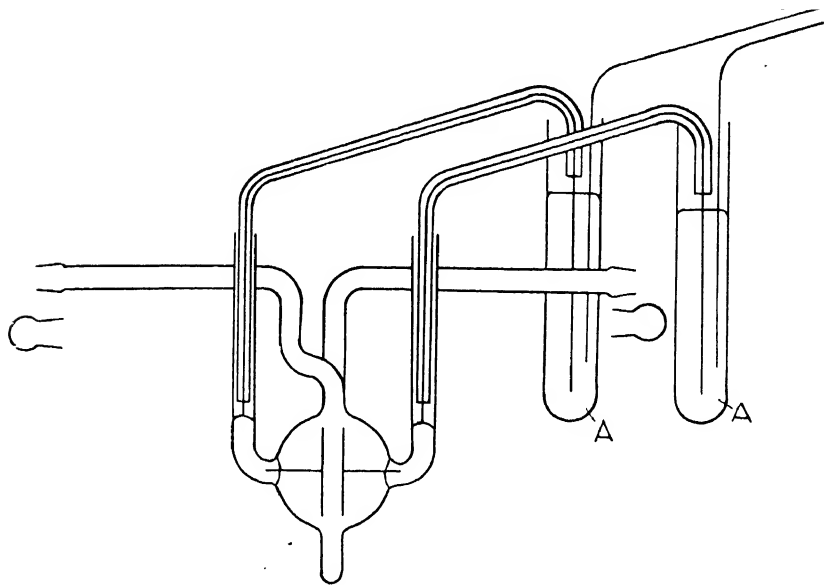

FIG. 23 (XI *)

iron and calcium, but a small amount of iridium is usually used to stiffen the platinum. In order that the value of the cell constant shall not alter, it is essential that the relative positions of the two plates shall not change
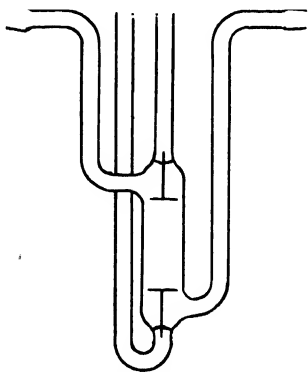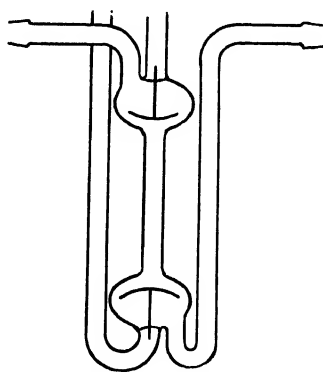

FIG. 24A (XI *)

FIG. 24B (XI *)

either by the bending of the plates or of the supports; the plates should therefore not be too thin and the supports should be as short as possible. The material of which the cell is constructed must be entirely unacted upon by the liquids used in it, and if possible its thermal properties should be such

that the cell constant is not affected by temperature changes. Ordinary glass is too soluble, and either Jena glass or quartz must be used. The difficulty of working the latter, the comparative fragility and cost of the cells, are such that Jena glass is generally used. Quartz is free from thermal hysteresis, which may possibly cause trouble with the cell constant of a glass cell when used at high temperatures. Whether the cell constant will vary with temperature depends on the dimensions of the cell and the expansion coefficients of the materials used. Washburn calculated that glass would be more satisfactory than quartz for the cells shown in Figs. 23 (XI *) and 24A (XI *), while quartz would be better for that in Fig. 24B (XI *).

The cells must not be connected directly to the bridge, in order to avoid loss of heat from the cell along the conductors. A method of making the connexion is shown in Fig. 23 (XI *). The bridge is connected by means of twisted lamp cord to the two mercury cups A which are placed in the thermostat. Each of these cups is then connected to one of the mercury cups on the electrolytic cell by means of an insulated and well amalgamated copper wire connector.

Shedlovsky[1] has designed a cell for the elimination of electrode effects. Jones and Bollinger[2] discuss the design of cells and Jones and Bradshaw[3] describe a method of calibration of cells which is now the accepted standard method : in the same paper they describe the redetermination of the conductance of KCl in absolute units.

Many cells suffer from error in design, thereby rendering them unsuitable for precision work.[4] It had always been assumed until the work of Parker[5] that the value of the cell constant was independent of the solution under measurement. Parker found variations as great as 0·33 per cent. Jones and Bollinger (loc. cit.) discovered that the so-called Parker Effect was due to placing the filling tubes of the cells too close to the electrical leads so that parasitic currents could flow through the capacity-resistance paths. Fig. 25A (XI *)[6] show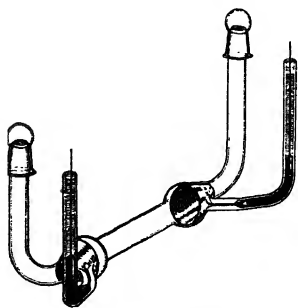s a cell so constructed to avoid this. A similar danger lies in the common use of dipping electrodes in which the electrical leads may be so near as to permit parasitic currents. These effects will, of course, be more marked with solutions of high resistance, and high frequencies. It is for these reasons that the flask cell shown in Fig. 25B (XI *) has its electrodes and leads taken out of the cell. The leads are widely separated and have between them the oil (used for accurate work) of the thermostat rather than the conducting solution.

FIG. 25A (XI *)

Cleaning Apparatus. All glass apparatus used in conductivity work must be very thoroughly cleaned before use. The apparatus used in the

[1] J. Amer. Chem. Soc., 1930, 52, 1806.   [2] Ibid., 1931, 53, 411.
[3] Ibid., 1933, 35, 1780.
[4] Jones and Bollinger, J. Amer. Chem. Soc., 1931, 33, 411.
[5] J. Amer. Chem. Soc., 1923, 45, 1366, 2017.
[6] D. Belcher, Thesis, Cambridge, 1937.

preparation of and as containers for conductivity water and the cells used in the measurements should first be well washed with warm chromic acid solution and then with distilled water. Finally they should be steamed for half an hour and set aside to drain dry. The steaming can conveniently be carried out by means of a glass flask containing distilled water and with a funnel with a stem of wide bore fitted into a cork in the neck; the steam passes through a vertical tube fitted into the stem of the funnel with a piece of rubber tubing. The vessel to be steamed is hung on the top of the glass tube and the condensed water is caught in the funnel.
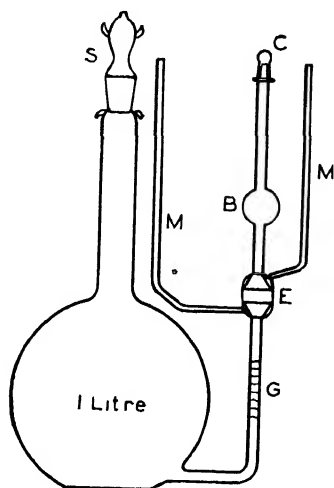

FIG. 25B (XI *)

Platinizing the Electrodes. Except with very low conductivities—less than 4×10^{-4} reciprocal ohms—it is necessary to eliminate polarization of the electrodes. The effect of polarization is to give a bad minimum in the telephone. A considerable range of silence is obtained, the note heard on the two sides of the minimum has not quite the same tone, and the point of balance found in the absence of polarization is not at the same point as the centre of the minimum when polarization is present. Polarization is eliminated by an increase in the frequency of the current and by platinizing the electrodes. It has already been stated that too high a frequency increases the effects of capacity and inductance, while thick layers of platinum black may cause changes in the solution owing to catalytic action or selective adsorption, and by the difficulty of completely washing out all traces of previously used solutions. For these reasons the frequency and the thickness of the platinum black must not be unduly increased, but only to such an extent as to bring about the desired result, namely, the elimination of polarization. The value required for this purpose can only be found by trial. In cases where platinum black is known to act on the solution an increase in frequency alone has to be relied upon. In other cases, except with the most concentrated solutions, platinizing alone is sufficient. Palladium black is generally considered more effective than platinum black at high concentrations, and Whetham says that platinum black heated to dull redness, so as to form grey platinum, reduces effects of occlusion. The effectiveness of platinum black is partly due to the very great increase in the area of the electrodes, and possibly is in part due to an accelerating effect in the reversal of the chemical changes due to the current. To platinize the electrodes they are first thoroughly washed with a warm chromic acid solution and then several times with distilled water. The platinizing solution consists of 3 grams of chloro-platinic acid and 0·02–0·03 grams of lead acetate dissolved in 100 ml. of water. The electrodes are supported in the solution in an inclined position in order to facilitate the escape of gas, and are connected by way of a Pohl commutator to a 4-volt accumulator and a rheostat.

In order to get a good black velvety coherent deposit the evolution of gas should be slow and the current should be reversed every half-minute. A deposit of average thickness is obtained in about 15 minutes. The coating now contains occluded gases and liquid, and these can be removed by electrolysing a dilute solution of sulphuric acid in the cell for half an hour, reversing the current every minute. The cell is then washed with conductivity water and left filled with the latter until required. Since with thick deposits of platinum black it is very difficult to ensure thorough cleaning, it is as well to test this by making a determination with conductivity water, washing out the cell and making a second determination with a fresh sample of the same water. When it is necessary to remove the coating this can be done by electrolysing aqua regia in the cell for a few minutes, reversing the current every minute.

Calibration of the Slide-wire : Method of Strouhal and Barus. A piece of hard wood or ebonite, a little over a metre long, has eleven holes bored half-way through to act as mercury cups. A piece of manganin wire of resistance approximately equal to that of the slide-wire is cut into ten equal lengths and the ends of each length are soldered to a piece of thick copper wire. The resistance is then placed inside a glass tube and fixed in position by means of sealing-wax, so that only the copper wires project. These are bent at right angles and the ends are amalgamated ; the resistances are marked from 1 to 10 and are then placed with their ends dipping into the mercury cups. The two end cups are connected by two
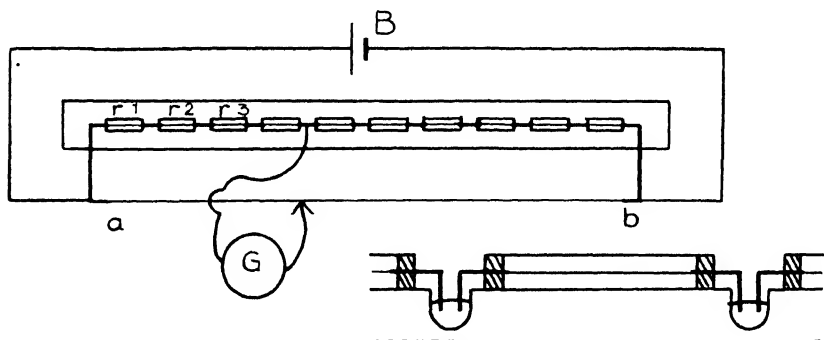
FIG. 26 (XI *)

thick amalgamated copper wires, one to each end of the slide-wire ; the ends of the slide-wire are also connected to a 2-volt cell. The sliding contact of the bridge wire is connected to the galvanometer and the free end of the other galvanometer wire is amalgamated to give contact with the mercury cups, as shown in Fig. 26 (XI *). The galvanometer lead is first put in cup 1 and the point of balance on the slide-wire found so that the galvanometer shows no deflection. Call the length of the slide-wire from the left to the point of balance 1 ; interchange resistances 1 and 2 and again find this point of balance l_1 ; next put the galvanometer in cup 2 (the order of the resistances being 2, 1, 3, 4, &c.) and find the point of balance l_2. Now 1 bears the same relation to the resistance of the whole slide-wire as r_1 does to the sum of the calibration resistances ;

and, similarly, the resistance of $l_2 - l_1$ bears the same relation to the resistance of the whole slide-wire as does r_1 to the total of the calibration resistances; that is, the resistance of 1 is equal to that of $l_2 - l_1$. Next interchange r_1 and r_3 (order 2, 3, 1, 4, 5, &c.) and find l_3; without altering the calibration resistances put the galvanometer lead into cup 3 and find l_4; the resistance of $l_4 - l_3$ is equal to that of 1. Proceed in the same way so that r_1 occupies all the cups in the calibration board in turn and until the galvanometer lead is in cup 9. This last reading subtracted from the total length of the wire gives the last length with a resistance equal to that of 1. Now add up all the lengths which have been found equal in resistance to 1; the sum will not be equal to the length of the slide-wire because the resistance of r_1 is not exactly one-tenth of that of the slide-wire. To compensate for this the sum of the lengths is subtracted from the length of the slide-wire and one-tenth of the value obtained is added (algebraically) to each of the measured lengths. Ten lengths are thus obtained, each of which has a resistance one-tenth of the total resistance of the slide-wire. The difference between these lengths and the scale readings gives the corrections which are to be applied to the slide-wire at the corresponding points. These corrections are plotted against scale readings on squared paper, so that the corrections at intermediate points can be determined. The example given (on following page) from Spencer (*Physical Chemistry*) will make the method of experiment and calculation clear.

The sum of the lengths in the fourth column is 998·3, and this subtracted from 1,000 leaves 1·7; one-tenth of this, i.e. 0·17, is added to each of the lengths given in column 4; the first length so obtained corresponds to one-tenth of the resistance of the wire, that is, to a scale reading of 100. The sum of the first and second lengths corresponds to a fifth of the resistance of the wire, i.e. to a scale reading 200, and so on.

Finally, it is an advantage to know the resistance of unit-length of the slide-wire. The relation of the resistance r_1 to that of the slide-wire is already known, so that, if the resistance of r_1 is balanced against that of a standard 1- or 10-ohm coil (according to which is nearer to the resistance of r_1) using the calibrated bridge, the actual value of the resistance r_1 can be found, and from this that of the whole slide-wire and of unit-length of it.

Manipulation of the Resistance Box. Resistance boxes are either of the dial type where the contact is made by a flexible metal bar pressing on a metal stud, or of the plug type where the contacts are made by metal plugs with insulating tops, the plugs being accurately ground to fit their seatings. Once the plugs have been ground in care should be taken not to mix them, by always placing a plug which has been removed from its seating in the hole provided in the brass bar, making it a rule to put each plug in the hole, say, to the left of its own seating. (It would be an advantage if the plugs were numbered.) The plugs should be kept very clean, especially avoiding dust, which will act as an abrasive and cause bad fitting, and grease, which will make bad contact. Grease can be removed with light petroleum. Manley found that lubrication of the contacts with a little vaseline reduces the contact resistances and also makes them less

Mercury cup connected to galv.	Arrangement of the resistances	Bridge reading	Length of slide-wire proportional to r_1	Corrected length of slide-wire	Length corresponding to 100, 200, etc.	Correction to be applied
1	$r_1 : r_2 \ldots \ldots r_{10}$	100·3	100·3	100·47	100·47	$-0·47$
1	$r_2 : r_1, r_3 \ldots r_{10}$	100·6				
2	$r_2, r_1 : r_3 \ldots \ldots r_{10}$	200·2	99·6	99·77	200·24	$-0·24$
2	$r_2, r_3 : r_1, r_4 \ldots r_{10}$	200·6				
3	$r_2, r_3, r_1 : r_4 \ldots \ldots r_{10}$	299·8	99·2	99·37	299·61	$+0·39$
3	$r_2 \ldots \ldots r_4 : r_1, r_5 \ldots r_{10}$	300·2				
4	$r_2 \ldots r_4, r_1 : r_5 \ldots \ldots r_{10}$	401·0	100·8	100·97	400·58	$-0·58$
4	$r_2 \ldots \ldots r_5 : r_1, r_6 \ldots r_{10}$	399·9				
5	$r_2 \ldots r_5, r_1 : r_6 \ldots \ldots r_{10}$	500·0	100·1	100·27	500·85	$-0·85$
5	$r_2 \ldots \ldots r_6 : r_1, r_7 \ldots r_{10}$	500·4				
6	$r_2 \ldots r_6, r_1 : r_7 \ldots \ldots r_{10}$	599·6	99·2	99·37	600·22	$-0·22$
6	$r_2 \ldots \ldots r_7 : r_1, r_8 \ldots r_{10}$	600·3				
7	$r_2 \ldots r_7, r_1 : r_8 \ldots \ldots r_{10}$	700·7	100·4	100·57	700·79	$-0·79$
7	$r_2 \ldots \ldots r_8 : r_1, r_9, r_{10}$	699·3				
8	$r_2 \ldots r_8, r_1 : r_9, r_{10}$	799·9	100·6	100·77	801·56	$-1·56$
8	$r_2 \ldots \ldots r_9 : r_1, r_{10}$	801·2				
9	$r_2 \ldots r_9, r_1 : r_{10}$	899·6	98·4	98·57	900·13	$-0·13$
9	$r_2 \ldots \ldots r_{10} : r_1$	900·3				
		1000·0	99·7	99·87	1000·0	$-0·00$

variable. Thus, with a dial box a reduction of 66 per cent in the resistance was obtained, while the variation was reduced from $\pm$ 66 per cent to $\pm$ 2·3 per cent ; with another box with seventeen plugs the total resistance was reduced 38 per cent and the percentage variation from $\pm$ 5·7 to $\pm$ 2·6. When not in use the plugs should rest loosely in their seatings and should be pressed firmly home when required for use. On removing a plug the one on either side should be again pressed home.

Calibration of Resistance Box. Method I. The resistances in a box can be calibrated in various ways and using either alternating or direct current. When required for use in conductivity measurements it is better to use the same source of current for the calibration as will be used later

on for the conductivity measurements. The two resistances to be compared are put in the two arms of the Wheatstone bridge, the battery or source of A.C. is connected to the point between the two resistances and to the contact-maker on the slide-wire, and the galvanometer or telephone is joined up to the two ends of the slide-wire. The point of balance having been found, the calibration correction is applied to the observed reading of the slide-wire, giving the corrected reading 1. If the length of the whole slide-wire is L, then

$$R_1/R_2 = 1/L - 1$$

or, again, the two resistances may be connected to the bridge by means of a commutator so that R_1 and R_2 may be interchanged, the point of balance is found, say, at 1, R_1 and R_2 are interchanged and the point of balance is now found to be at $1 + n$; then

$$\frac{R_1}{R_2} = \frac{L - n}{L + n}, \text{ or approximately } \frac{L - 2n}{L}$$

In making the calibration we may proceed either by taking a standard 10 ohms as the comparison standard, and so get the actual resistances of the various coils, or by assuming that the sum of all the resistances in the box is correct, as is done in calibrating a set of weights, where the sum of all the weights is assumed to be correct; and in this case we shall get the relative resistances of all the coils, which is all that is required in conductivity measurements using a cell constant. In the first case the standard 10 ohms is first compared with the sum of the 5, 2, 2*, and 1 ohms; then the 5 ohms is compared with the sum of 2, 2*, and 1 ohms, the 2 ohms with the 2* ohms and the 2* ohms with the 1 ohm. Suppose it is found that the standard

$$
\begin{aligned}
10 \text{ ohms} &= 5 + 2 + 2* + 1 + a \\
5 \text{ ,,} &= 2 + 2* + 1 + b \\
2 \text{ ,,} &= 2* + c \\
1 \text{ ,,} &= 2* + d
\end{aligned}
$$

Substituting in the first equation we find

$$10 \text{ ohms} = 6 \times 2* + a + b + 2c + 2d$$

This equation gives the correction to the 2* ohm coil; suppose this is e, so that

so that
$$2* = 2 + e \text{ ohms,}$$
then
$$
\begin{aligned}
1 &= 2 + e + d \\
2 &= 2 + e + c \\
2* &= 2 + e \\
5 &= 6 + 3e + b + c + d
\end{aligned}
$$

Next 10 will be compared with $5 + 2 + 2 + 1$

$$
\begin{aligned}
20 \text{ ,, ,,} \quad \text{,,} \quad \text{,,} \quad & 10 + 5 + 2 + 2 + 1 \\
20* \text{ ,, ,,} \quad \text{,,} \quad \text{,,} \quad & 20 \\
50 \text{ ,, ,,} \quad \text{,,} \quad \text{,,} \quad & 20 + 20* + 10, \text{ and so on.}
\end{aligned}
$$

Some boxes are provided with holes in the brass blocks to take the plugs when they are removed from their seatings between the blocks, and an additional plug with a terminal is provided. This makes a very

satisfactory way of making the connexion to the box, but, failing this, a screw clip with a terminal attached may be used.

Method II. In the second method, when the sum of the resistances is supposed to be correct, the connexions can be made as shown in the
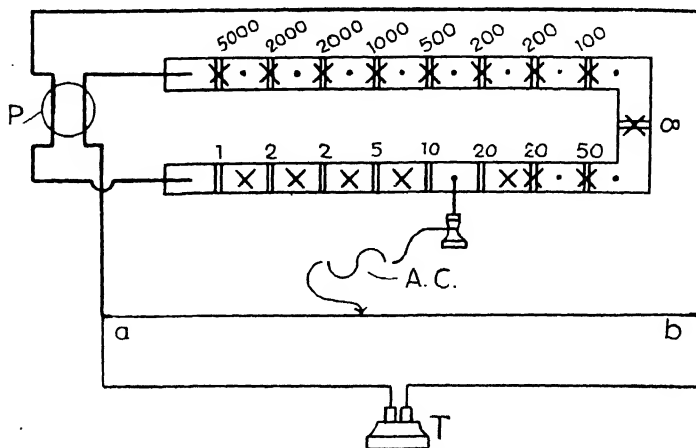

FIG. 27 (XI *)

diagram (Fig. 27 (XI *)). In different boxes the resistances are given different values; in one case the arrangement is

> 5,000 2,000 2,000* 1,000 500 200 200* 100
>   50   20   20*   10   5   2   2*   1

Here the comparisons would be made

$$5,000 = 2,000 + 2,000* + 1,000. + a$$
$$2,000 = 2,000* + b$$
$$2,000 = 1,000 + \text{rest of smaller resistances} + c$$
$$1,000 = \text{rest} + d.$$

Another arrangement is

> 5,000 2,000 1,000 1,000* 500 200 100 100*
>   50   20   10   10*   5   2   2*   1

The scheme here would be

$$5,000 = \text{rest} + a$$
$$2,000 = 1,000 + 1,000* + b$$
$$1,000 = 1,000* + c$$
$$1,000 = \text{rest of smaller resistances} + d.$$

A third arrangement is

> 4,000 3,000 2,000 1,000 400 300 200 100
>   40   30   20   10   4   3   2   1

the comparisons being

$$4,000 = 3,000 + 1,000 + a$$
$$3,000 = 2,000 + 1,000 + b$$
$$2,000 = 1,000 + \text{rest} + c$$
$$1,000 = \quad + d.$$

The calculations would be made in the same manner as described in the section dealing with the calibration of a set of weights.

Assembling Apparatus. In assembling the apparatus for the conductivity measurements every care should be taken to keep the two arms of the bridge as far as possible symmetrical with each other and with the slide-wire and the earth (as shown in Fig. 28 (XI *)) ; the connexions should be made with straight flexible wire, equal lengths being used in each arm of the bridge so that they will balance out. The slide-
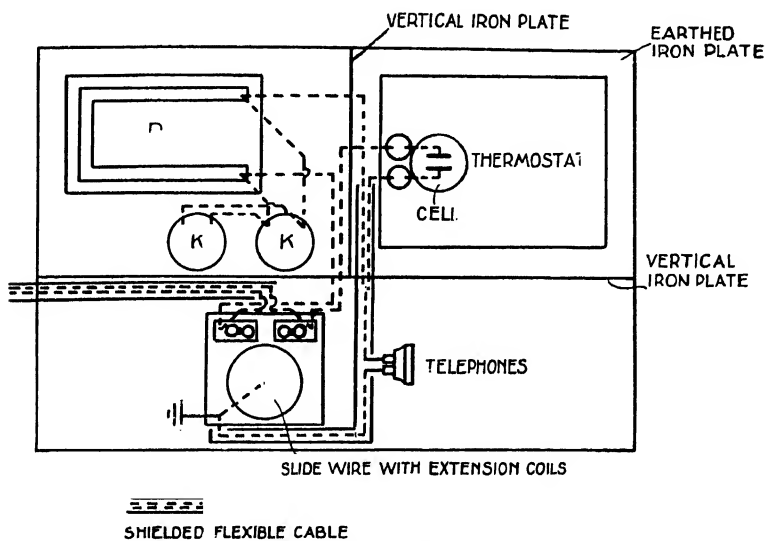

FIG. 28 (XI *)

wire, resistances, condensers and thermostat should all be placed on a large sheet of iron which is connected to an earth-plate and vertical sheet-iron plates between the resistance box and the thermostat containing the electrolytic cell and between these and the slide-wire. The source of current should not be too near and should stand on an earthed plate. The connexion to the bridge should be by means of shielded flexible cable with the metal coating connected to earth, the same material being used for the telephone connexions.

The Control of Industrial Processes by Conductivity. The control of processes by conductivity is not so general as control by pH, due largely to the lack of suitable apparatus. Such an apparatus is now available from the Cambridge Scientific Instrument Co. The conductivity of a solution is due to the sum of the conductivities of all the ions present, so that on neutralizing sulphuric acid with caustic soda, the conductivity does not fall to that of pure water but to that of a solution of sodium sulphate. Use is therefore made of a comparison or reference cell in addition to the test cell. Both cells are arranged to have the same constants and dimensions so that they respond similarly to temperature changes : this is important because the conductivity alters by 2–3 per cent per degree. The test cell has ports which allow the liquid under test to circulate freely : the com-

parison cell is closed and contains a sample of the liquid in the bath adjusted to the required concentration, e.g. 5 per cent sulphuric acid to take a simple case.

To measure the conductivity a modified form of Wheatstone bridge is used, arranged to operate at a frequency of 800–1,000 cycles per second and balance is indicated by the disappearance of the 800-cycle note in a telephone. The bridge may be operated by batteries or for continuous work from the mains. By means of a change-over switch the bridge may be arranged to read directly in resistance (ohms) or in conductance (ohms) and by the operation of another switch the test cell is connected to the reference cell, the ratio of the two cells being shown on a dial : for a given solution, e.g. sulphuric acid, the dial may be calibrated to read off the concentration of the test solution : or tables may be prepared for any solution.

Examples of the use of the apparatus are the measurement of chloride contamination of boiler feed water and the determination of the concentration of sulphuric acid in the acid tower of a contact process plant. In the first case the reference electrode is filled with uncontaminated feed water and in the second the cell contains 98·4 per cent sulphuric acid and the instrument is calibrated to read grains of sodium chloride per gallon or percentage of sulphuric acid respectively. As in the case of pH the apparatus can be adapted to automatic control.

Ordinary distilled water generally has a conductivity of well over 2×10^{-6} reciprocal ohms, and with a dilute solution this represents a considerable percentage of the total conductivity ; purer water is required for accurate work. The purest water that has been prepared was obtained by Kohlrausch and Heydweiller, who by re-distillation *in vacuo* forty-two times at length obtained a specimen having a specific conductivity of $0·043 \times 10^{-6}$ at 18° and $0·015 \times 10^{-6}$ at 0°. They estimated that absolutely pure water would have a conductivity of $0·0384 \times 10^{-6}$ at 18°. Water with this very low conductivity can only be kept in the absence of air. The same workers showed the effect of exposure to air by the following results :

Conductivity of original specimen *in vacuo* . . $0·05$ to $0·11 \times 10^{-6}$
,,   after 20 minutes' exposure to air . $0·34$ to $0·40 \times 10^{-6}$
,,   after long exposure to air . . . $0·65$ to $0·70 \times 10^{-6}$

Thus even a short exposure to air produces a very great increase in the conductivity. Kendall found that the conductivity of water saturated with carbon dioxide under atmospheric conditions was $0·75 \times 10^{-6}$ reciprocal ohms, a result which makes it almost certain that the rise in conductivity on exposure to air is due to the absorption of carbon dioxide, a conclusion which is still further strengthened by the fact that the conductivity of water can be very considerably lowered by bubbling carbon-dioxide-free air through it. Pure carbon-dioxide-free water is so unstable in the presence of air that for most purposes it is better to aim at preparing a water free from all impurities except carbon dioxide only, i.e. water having a conductivity of $0·7$ to $0·8 \times 10^{-6}$ reciprocal ohms, and to apply the necessary correction for this to the determined conductivities of the solutions made up with it.

Preparation of Conductivity Water. The difficulty of obtaining

good-conductivity water varies considerably in different laboratories. The preparation must be carried out in a room free from chemical fumes, and containing vessels of well-aged Jena or other resistance glass which have been thoroughly steamed should be used. The flasks may be closed with paraffined corks fitted with a soda-lime tube. The most important impurities in ordinary distilled water appear to be ammonia and carbon dioxide. In many cases a very fair water can be obtained by a distillation in glass apparatus of distilled water which has been allowed to stand for a time with acid permanganate, followed by a redistillation with the addition of sodium or barium hydroxide, using a block tin condenser and only collecting the middle fraction. Kendall found that a little Nessler's
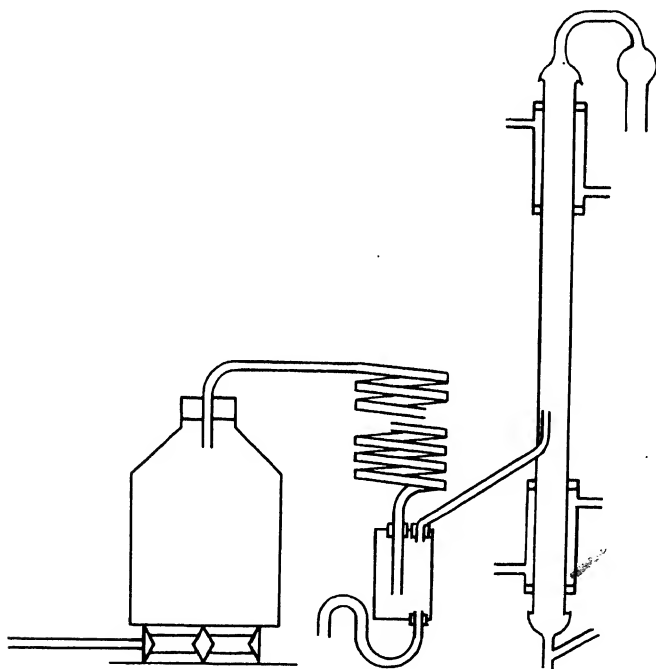

FIG. 29 (XI *)

solution was very effective in retaining ammonia. Bourdillon describes an apparatus for preparing very pure water by a single distillation. The apparatus which is shown in Fig. 29 (XI *) consists of a copper boiler holding 13 litres and closed with a rubber stopper through which passes a copper tube 1·3 cm. in external diameter and 8·5 metres long. The tube is coiled into a spiral of nineteen turns and the end of it passes into a spray trap consisting of a copper cylinder with an exit tube for the condensed spray at the bottom and a side-tube of tin for the steam. The spray trap and the copper coil are well jacketed with cotton waste and about 20 per cent of the steam condenses in them. The steam leaving the trap passes upwards into a tin tube 2·5 cm. in diameter and 145 cm. long, entering at a point 45 cm. from the bottom. The tin tube has glass condensers sur-

rounding the top and the bottom ; the top is closed with a tin cap fitted with a soda-lime tube and the bottom with a tin cap with an exit tube for the water at the bottom and a side-tube through which a stream of purified air enters at the rate of about 4 litres per hour. The boiler is filled with distilled water to which 5 grams of acid potassium sulphate or phosphoric acid are added. The steam passes up the tin tube and is condensed at the top. As the water passes down the sides it meets the incoming steam and the purified air and these remove dissolved gases ; the bottom condenser serves to cool the water down to the desired temperature. Distillation is carried out at the rate of about 1·2 litres per hour. The conductivity of the water rapidly falls and an hour after the start reaches a value of 0·11 to 0·09 × 10^{-6} reciprocal ohms.

Water of this purity can be obtained until all but 3 litres have been distilled over, when it is desirable to stop. Nothing is gained by using such pure water unless the cell is airtight, and even then the conductivity gradually rises.

Weiland has shown that it is possible to obtain water having a conductivity of from 0·05 to 0·07 × 10^{-6} reciprocal ohms by means of a single distillation of conductivity water of 0·6 to 0·8 × 10^{-6} reciprocal ohms. About 13 litres of the water was kept in a quartz flask at a temperature a few degrees below its boiling-point, while a stream of carefully purified air was passed through for about 20 hours. This carries out practically all the dissolved gases, and on distilling through a block tin condenser into a quartz cell the very pure water was obtained.

Determination of the Cell Constant. The next step consists in the determination of the cell constant. For this purpose a solution of potassium chloride is used of such a concentration as has a conductivity of the same order as those to be measured in the cell. The particular strength required can be seen from the accompanying table taken from the results of Kohlrausch. The conductivities are given in reciprocal ohms per centimetre.

Temp.	N	N/10	N/50	N/100
0°	0·06541	0·00715	0·001521	0·000776
5	0·07414	0·00822	0·001752	0·000896
10	0·08319	0·00933	0·001994	0·001020
15	0·09252	0·01048	0·002243	0·001147
18	0·09822	0·01119	0·002397	0·001225
20	0·10207	0·01167	0·002501	0·001278
25	0·11180	0·01288	0·002765	0·001413
30		0·01412	0·003036	0·001552
32·5		0·01475	0·003174	0·001623
35		0·01539	0·003312	

Suppose that an N/10 solution is to be used and the measurements to be made at 18°. The molecular weight of potassium chloride, according to modern atomic weights, is 74·56, but since Kohlrausch took the value 74·59, his N/10 solution would contain 7·459 grams per litre. Correcting for the buoyancy of the air, this becomes 7·4555 grams. This quantity of the pure dry powder is therefore weighed out and made up to 1 litre with conductivity water at 18° ; it is generally desirable to weigh both solute and solvent. Next, to make sure that the cell is quite clean, it is filled with conductivity water and placed in the thermostat. After allow-

ing it to remain there from 15 to 20 minutes, so that it may reach the temperature of the bath, the resistance is measured. 5 minutes later the resistance is again determined; if the cell had reached the temperature of the bath this will be the same as before. The cell is then washed with conductivity water, refilled, and its resistance again determined; a constant value shows that the cell is clean. Next, the cell is thoroughly washed with the solution, filled, and replaced in the bath; the temperature of the latter requires to be steady to 0·001°, since the temperature coefficient of conductivity of electrolytes is so high, being about 2 per cent for ordinary solutions and 5 per cent for water. After allowing the cell to remain for 15 minutes, the current is turned on and the resistance in the box altered until the point of balance is obtained near the middle of the bridge. Next, adjust the condensers until a sharp minimum is obtained. During these adjustments it is possible that the cell has been warmed up by the measuring current, so the circuit is opened for 2 minutes and then closed and the final bridge setting made. The circuit is again left for 10 minutes and another reading taken. The cell is refilled and the measurements are repeated with a different rheostat resistance. Suppose that the resistance is found to be R ohms in the particular case, with N/10 potassium chloride, then the cell constant K is equal to R × 0·01119, since 0·01119 is the specific conductivity of this solution. Then, if the resistance of the cell filled with another solution is found to be R′, the conductivity C of this solution will be K/R′.

Effect of Platinized Electrodes. As indicated earlier, Taylor and Acree have shown that while with platinized electrodes of an inch or more in diameter and a resistance of not less than 100 ohms the true resistance is obtained, this is not the case with bright electrodes. The resistance at 1,000 cycles is less than that at 600 cycles by from 0·11 to 2·6 per cent. The change of resistance with change of frequency is decreased by an increase in the resistance, i.e. by a decrease in concentration and by a change in the area of the electrodes. Since the ratio of the conductivities of two solutions at infinite frequency in a cell with bright electrodes (the ratio at infinite frequency being obtained by extrapolation of the ratios determined at a number of known frequencies) approximates very closely to the ratio obtained with the same solutions in a cell with platinized electrodes, the resistance at infinite frequency may be assumed to be the true resistance in the former case. The relation is given by

$$R_f - R_{f\infty} = KL_f f$$

where $R_{f\infty}$ and R_f are the resistances at infinite frequency and frequency f, K is a constant (0·00182) and L_f is the inductance in millihenries at frequency f. The equation shows that the 1,000 cycles R_f will not differ from R by more than 0·01 per cent if the solution is so dilute that L_f is less than $0·5 × 10^{-4}$ times the resistance. The concentrations which can be used in a given cell, so as to get the true resistance, can thus be found from this relation, or the same result can be obtained by determining what resistance in the cell is required to make the difference between the resistances determined at frequencies 500 and 1,000 cycles less than 0·01 per cent.

Technical Application of Conductivity Measurements. A useful

technical instrument for examining water by the conductivity method is the Dionic Water Tester made by Evershed and Vignoles, and shown diagrammatically in Fig. 30 (XI *). The instrument contains its own generator and current-measurer, which are on the same principle as in the well-known Megger testing sets. E is a continuous-current dynamo driven by the handle W. The dynamo is fitted with a constant-speed clutch which slips when the dynamo handle is turned above a certain speed. With the aid of this device the voltage is maintained at 100 ± 0.25 volts. The current passes by means of the electrodes A and B through the solution
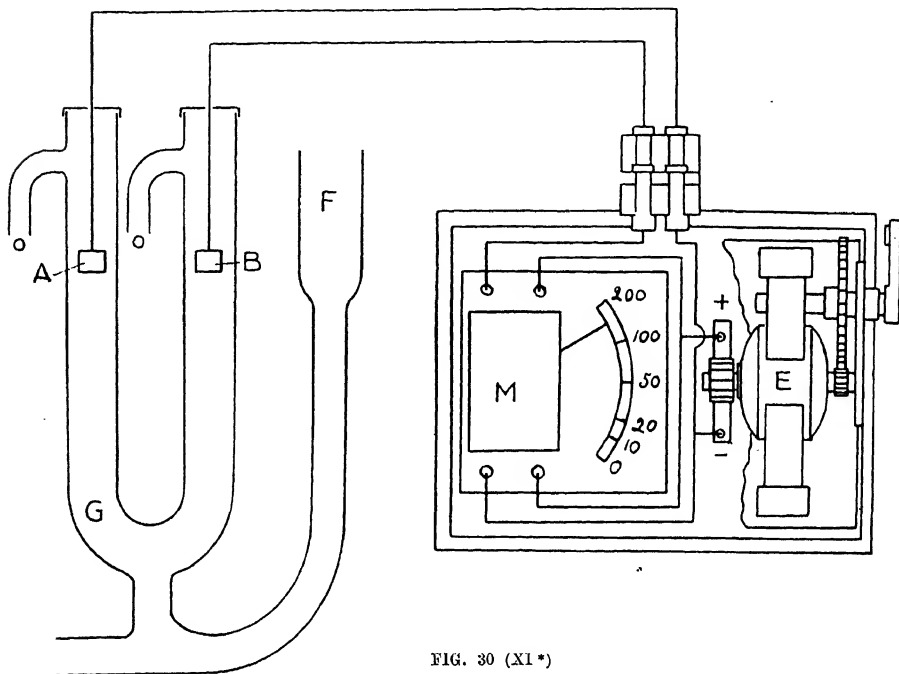

FIG. 30 (XI *)

contained in the U-tube G and then through the conductivity meter M. The current used is not more than 0·004 amp. and is not applied for more than 2 or 3 seconds, but this is sufficient time for the maximum E.M.F. of polarization to be set up. Allowance is therefore made for the back E.M.F. in the calibration of the meter M, which reads from 0 to 2,000 reciprocal megohms. In addition, a switch is provided which multiplies the scale reading by 10, thus giving the range 0 to 20,000 units. An additional tube can also be obtained in place of G, designed for use with sea water of which the conductivity is approximately 50,000 units, but which can of course be used for other solutions. To correct for the effect of temperature either of two devices may be used. The instrument is calibrated for 20°; if the temperature is between 10° and 40° the conductivity at 20° is given by

$$K_{20} = M_t \times \frac{100}{56 + 2.2t}$$

where M_t is the meter reading and t is the Centigrade temperature.

The alternative device is a thermometer, which is fitted inside the arm A of the conductivity tube and which has attached to it a metal index moving over a scale of temperatures attached to the wooden support of the U-tube. The thermometer reading is taken and the thermometer is then moved up or down until the index points to the temperature reading on the fixed scale. The effect of moving the thermometer down is to decrease the conductivity by displacing some of the solution, and this is so arranged as to compensate for the effect of temperature, so that the reading of the meter gives directly the conductivity at 20°. In carrying out a test the solution is poured into F until it runs out of the side-tubes O, a fair quantity of solution being allowed to run out of O and also out through the pinch-cock at the bottom. The thermometer is read and adjusted, and the handle W then turned clockwise at a speed of 80 to 100 r.p.m., or until the clutch is found to slip, when the needle of the meter M will be found to come to rest and the conductivity can be read off. The tube is then at once washed out with distilled water. The instrument has been used with success in the determination of total solids in water, the control of water softening, testing for leakages in condensers and pipe-lines, and in testing for pollution of rivers by sewage effluents.

Conductometric Titrations. This method offers certain advantages in some cases, as for example with coloured or turbid solutions, neutralizations of weak acids with weak bases and titrations of extremely dilute solutions. The method has not been largely used owing to the troublesome nature of the series of conductivity measurements required. A simplified method has recently been devised [1] in which the time required for the complete titration is reduced to about 20 minutes. The apparatus used is a modified form of the conductivity meter of the Dionic Water Tester (Fig. 30 (XI *)) ; this meter has a range from 0 to 200,000 reciprocal megohms ; instead of the tube G the electrodes A and B stand in a circular glass trough 20 cm. in diameter and 12 cm. high. On the top of this rests a piece of ebonite 23 cm. long, 4·5 cm. wide and 1 cm. thick ; it is prevented from slipping by two small screws projecting 1·3 cm. below and fitting just inside the edges of the trough. The electrodes are of bright platinum foil 0·7 cm. by 2·0 cm. and are sealed into glass tubes 16 cm. long. These tubes fit tightly through holes 17·5 cm. apart in the ebonite and are fixed by means of sealing-wax. The bottoms of the electrodes are near the bottom of the cell. A glass stirrer in the shape of an L with the horizontal part 5 cm. long is placed at one side of the titration cell so that it just clears the side of the glass and is equidistant from the two electrodes ; the stirrer is turned by a small electric motor at a speed of about 150 r.p.m.

Method. 20 to 25 ml. of the solution to be titrated are measured out into the glass vessel ; a litre of distilled water is then added ; the stirrer is started and the first reading is taken by turning the handle of the meter till the clutch just slips and then reading the position of the pointer on the scale. The titrating liquid in the burette is adjusted exactly to the zero and the adhering drop of liquid removed from the jet by touching with a glass rod. The liquid in the burette is then run down exactly to 4 ml. into the glass vessel ; the adhering drop being removed by a glass

[1] Rae, *J. Chem. Soc.*, 1931.

rod which stands in the titrating cell when not in use ; in this way an exact volume of reagent is added which facilitates plotting. Without stopping the stirrer (this keeps the electrode free from gas bubbles), the conductivity reading is taken at once. The liquid is run down in turn to 8, 12, 16, &c., ml. and the process repeated until a sufficient number of readings has been taken. The results are plotted on squared paper with the observed conductivities as ordinates and the number of ml. of reagent added as abscissae. The intersection of the two lines so obtained gives the endpoint. The dimensions of the apparatus have been so chosen that N/10 solutions can be used. Temperature changes are found to be negligible and the increase in the total volume due to the addition of the reagent does not materially affect the result. The method is useful both for precipitation and neutralization reactions.

Theory. In outline the theory of the method for neutralizations is simple. If we take 10 ml. of N/10 hydrochloric acid and dilute it to 1 litre, we have 1 litre of N/1,000 acid solution ; at this dilution we may assume complete dissociation of acid, alkali and the salt formed. At the start we have hydrogen ion and chloride ion present, the ionic mobilities of these at 18° (Kohlrausch) are 315 and 65·5, total 380·5 and the actual conductivity of the solution will be 380·5 C where C is the constant for the cell and an N/1,000 solution : when 10 ml. of N/10 potassium hydroxide has been added, all the acid has been converted into potassium chloride solution and this (ignoring the increase in volume) is present in N/1,000 solution ; the ionic mobilities of the two ions being 64·6 and 64·5, total 130·1, the actual conductivity will now be 130·1 C. When 20 ml. of alkali, i.e. an excess of 10 ml. has been added, the solution will consist of N/1,000 potassium chloride, together with N/1,000 potassium hydroxide : the mobility of the hydroxyl ion being 174, the conductivity due to the alkali will be (64·6 + 174) C, i.e. 238·6 C, to which must be added 130·1 C for the potassium chloride, giving a total of 338·7 C. During the titration then, the conductivity starts at 380·5 C, falls to 130·1 C when neutralization is complete, and rises to 338·7 C when one equivalent excess of alkali has been added.

In the titration of sodium chloride with silver nitrate, the initial conductivity is that due to the sodium chloride : when a little silver nitrate is added, some of the chloride is precipitated as silver chloride and the corresponding amount of sodium is converted into sodium nitrate ; the conductivity of this sodium nitrate differs but little from that of the sodium chloride it has replaced, so that the titration curve is nearly parallel to the X axis while the precipitation proceeds. After the endpoint has been passed, the excess of silver nitrate added remains in solution and so the conductivity now shows a steady increase.

Example of the titration of 24·99 ml. of 0·10205 N.HCl with 0·0966 N.NaOH. 1,100 ml. of distilled water.

ml. of alkali added	Meter reading	ml. of alkali added	Meter reading	ml. of alkali added	Meter reading
0 .	136,000	20 .	63,500	35 .	66,000
5 .	117,500	25 .	46,000	40 .	79,000
10 .	99,500	27 .	43,000	45 .	93,000
15 .	81,000	30 .	51,000		

The intersection of the two lines of the titration curve gives the endpoint as 26·36 ml. so that the calculated concentration of the alkali is 0·09675 N.

Titration of 20 ml. of 0·1002 N.NaCl with 0·1005 N.AgNO$_3$. 1·5 litres of distilled water.

ml. of AgNO$_3$	Meter reading	ml. of AgNO$_3$	Meter reading	ml. of AgNO$_3$	Meter reading
0 . . .	34,500	14 . . .	33,800	26 . . .	41,400
2 . . .	34,500	16 . . .	33,500	28 . . .	44,500
4 . . .	34,500	18 . . .	33,500	30 . . .	47,300
6 . . .	34,200	19 . . .	33,300	35 . . .	54,500
8 . . .	34,200	21 . . .	34,600	40 . . .	61,000
10 . . .	34,200	22 . . .	35,800		
12 . . .	34,000	24 . . .	38,500		

The endpoint is 20·24 ml. and the calculated normality of the silver nitrate 0·0990 ; this value is low because of the solubility of the silver chloride : if this is allowed for, a value very close to the correct one is obtained. Under favourable circumstances the accuracy of the method is 1 in 400.

HYDROGEN-ION CONCENTRATION

SECTION 1: ELECTROMOTIVE FORCE MEASUREMENT

THE Principle of E.M.F. Measurements. This can be explained by means of Fig. 1 (XII *), in which E is a source of steady E.M.F., which sends a current along the resistance AB ; there will thus be a fall of potential along the wire AB, and the potential difference between the points A and b for a steady current will depend on the resistance between those points. If a second source of E.M.F. e_1, which is smaller than E, is connected as shown to A and through the key K and the galvanometer
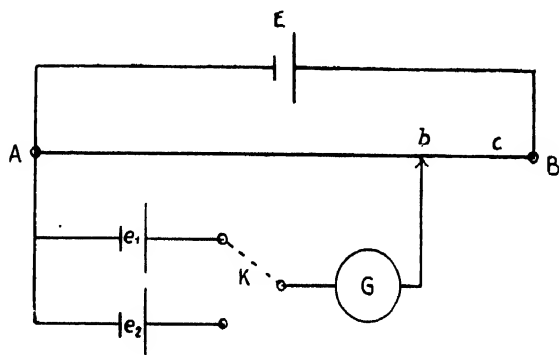
FIG. 1 (XII *)

G to a contact b on AB, there will be no flow of current through the galvanometer when the PD between A and b is equal to e_1, the E.M.F. of the cell; the position of b can thus be found experimentally. In a similar way with another cell e_2 a position c can be found for the contact so that the P.D. over Ac just balances e_2 and no current flows. Then

$$\frac{e_1}{e_2} = \frac{\text{P.D. for A to } b}{\text{P.D. for A to } c} = \frac{\text{Resistance A}b}{\text{Resistance A}c}$$

Thus, if the value of e_2 is known, that of e_1 can be obtained. It will be seen that the measurement depends upon (1) a steady source of E.M.F. E, or a steady current; (2) a standard of E.M.F. e_2; (3) a knowledge of the ratio of the resistances of Ab and Ac. In the earliest form of potentiometer AB consisted of a wire of uniform resistance so that the resistances were proportional to the lengths.

Potentiometers. Fig. 2 (XII *) shows a diagram of the Compton potentiometer in which AB represents 14 coils, each of which is 10 ohms

resistance.   BC is a slide-wire of uniform resistance and also having a total resistance of 10 ohms.

E is the source of E.M.F. and R_1 and R_2 are resistances which act as rheostats, giving a coarse and a fine adjustment respectively. If by means of the rheostats the P.D. between AC is reduced to exactly 1·5 volts, the P.D. of each coil between A and B will be 0·1 volt, and that between B and C also 0·1 volt; further, if BC is a metre wire divided into millimetres each millimetre will have a P.D. of 0·0001 volt. ✓

G is a sensitive galvanometer, H a contact key, and K a switch, so that a standard cell or the cell whose E.M.F. is to be measured can be switched in at will. The instrument is set by means of the standard cell. If this be a Weston, giving an E.M.F. of 1·0183 volts, and the contacts were set as shown, the total P.D. between AC being 1·5 volts, the P.D. between P_1 and P_2 would be 1·0183 volts, 1 volt between P_1 and B, and 0·0183 volt between B and P_2, and no current would flow through G. The
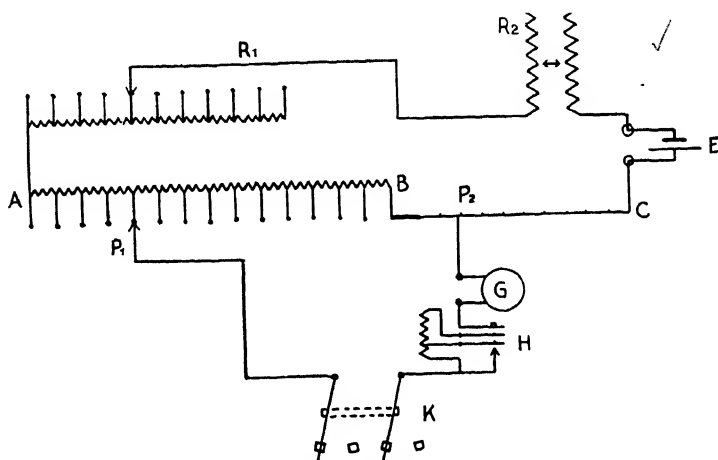

FIG. 2 (XII *)

setting of the instrument is made by making the contacts P_1 and P_2 at the start so that the indicated reading on the coils and the slide-wire is equal to the E.M.F. marked on the standard cell, and then by means of the rheostats R_1 and R_2 altering the voltage between AC and therefore P_1P_2 until the galvanometer shows no indication of current on depressing the key H. The potentiometer is thus set so that its readings indicate volts and the E.M.F. of another cell can be measured directly by switching over the key K and altering P_1 and P_2 until on momentarily depressing H no current flows through G. The E.M.F. is then read off directly from the number of 0·1 volt coils, and the length of the wire BC included between P_1 and P_2 when balance has been obtained. After taking the reading the correctness of the setting of the potentiometer is checked by switching K over to the standard cell and seeing that balance is obtained when P_1 and P_2 are in such a position as to give the marked voltage of the cell.

Fig. 3 (XII *) represents the Leeds and Northrup potentiometer. Between the points A and D are fifteen coils each of exactly 5 ohms resistance,

and between B and D is a wire a little over 200 inches long wound in eleven turns on a drum 6 inches in diameter ; the first ten turns of this wire have a total resistance of 5 ohms, and since each turn is divided into 100 scale divisions, one scale division is equal to a resistance of 0·005 ohm. By means of the two contacts M and M' any number of the 5-ohm coils and any length of the extension wire can be connected through the galvano-meter G and the key U to the cell E. The current from a single accumu-lator W flows through the regulating rheostat R, the resistance coils AD and the slide-wire DB, and also through the additional coils shown between OA. When the current is reduced by means of the rheostat in the manner
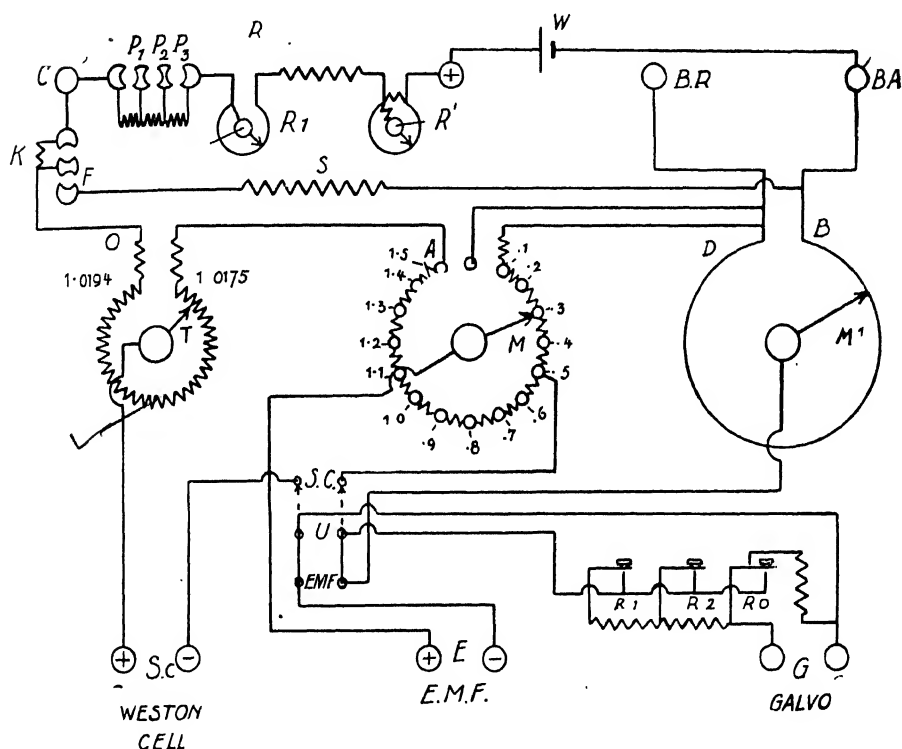

FIG. 3 (XII *)

to be described, to 0·02 amp., the fall of potential across each of the 5-ohm coils will be exactly 0·1 volt and along each scale division on the wire DB will be 0·0001 volt. The setting of the instrument so as to produce the correct current to give this result is carried out in the first instance by connecting a Weston cell at the point E. Suppose this cell to have an E.M.F. of 1·0185 volts, the contact M is moved round to the tenth stud, marked 1·0, and the contact M' to the 185 scale division. The plug is inserted in K to short-circuit this resistance ; when a freshly charged accumulator is used the plugs at P are left out and as the cell runs down the resistances P_1, P_2 and P_3 are short-circuited in turn. In making the first trial the galvanometer key R_1 is used so as to include a high resistance

in the galvanometer circuit and prevent a large current flowing through the standard cell. The dial R_1 is then used to make a coarse adjustment of the resistance and R' to make a fine adjustment, the keys R_2 and R_0 being used with the galvanometer as balance is approached more closely. When the galvanometer shows no deflection on making contact with R_0, the E.M.F. of the cell is balanced against the drop of potential between the contacts M and M', and the instrument is set to read voltages directly. An unknown E.M.F. can now be inserted at E, and M and M' be adjusted so as to give no current through the galvanometer; in testing, the key R_1 will always be used first and finally R_0. In order to make sure that the potential drop between AB does not change during the course of the measurements, the additional dial and contact T, together with a change-over switch at U, are provided. One of the terminals SC of the switch U is permanently connected to the fifth stud between AD; the other terminal is connected through the galvanometer to the standard cell at SC and so to the terminal T which moves round a dial with twenty studs corresponding to the E.M.F. between 1·0175 and 1·0194 by steps of 0·0001 volt. T is turned to the voltage marked on the cell (in the example 1·0185 volts) and the resistances between the studs are so adjusted by the makers that when the instrument has been correctly set by the first method and the Weston cell has then been moved to SC and T adjusted as described, no current will flow through the galvanometer. If during the course of the experiment any change of voltage occurs between AB, a corresponding change will occur between T and the 0·5 stud; the steadiness of the potential drop can therefore be tested readily during the course of the experiment by switching U over to SC and observing whether a current flows through G. If it does the rheostat R must be altered to bring the P.D. back to the correct value. In measuring an unknown E.M.F. this is connected at E, and M and M' are adjusted till balance is obtained as shown by the absence of deflection in the galvanometer, the switch U is then at once turned over and the correctness of the setting of the potentiometer verified before the reading is taken.

Measurement of Low Potentials. When the E.M.F. to be measured is less than 0·15 volt the low scale can be brought into use. This is done by means of the resistances K and S. The instrument is set with the standard cell as before so that the total current is 0·02 amp.; when the plug at F is inserted the resistance S shunts the resistance between OB so that only one-tenth of the current passes along OB. The effect of introducing the shunt is to reduce the total resistance between F and B so that it is necessary to introduce an additional resistance K to balance this reduction and so to maintain the total current at its former value. The removal of the plug from K and its insertion in F therefore reduces the drop of potential over each pair of plugs in M from 0·1 to 0·01 volt and so enables readings to be taken down to 0·000005 volt. To enable the resistance coils in M to be checked, each brass block is bored so that a plug terminal can be inserted; each coil can then be compared with a 5-ohm coil by means of a Wheatstone bridge and the equality of the coils be verified with great simplicity. Connexions are provided for calibrating the slide-wire with the aid of the coils in M.

The terminals BA and C are connected by a thick copper wire. E is also short-circuited. The galvanometer is connected at G and the battery between BA and BR. On turning the switch down to E.M.F. the contacts M and M' are connected through the galvanometer. There is a fall of potential from D round the wire to B, and round the coils to A and O, so that the wire can be calibrated into sixteen parts of equal resistance since the total resistance between A and O is also 5 ohms. K is short-circuited during the calibration. This potentiometer can also be used to measure voltages up to 16 volts. For this purpose the plug is inserted at F and a battery of 20 volts applied at W. With the standard cell the setting is made as already described by means of the rheostat R; the voltage drop between AB is now 1·6 volts, but on removing the shunt plug from F to K this rises to 16 volts.

The Standard Cell. The Weston cell is generally used on account of its low temperature coefficient. The E.M.F. of the normal Weston cell is 1·0183 international volts at 20°, and its E.M.F. at $t°$ is given by

$$E_t = E_{20} - 0·0000406 \ (t - 20) - 0·00000095 \ (t - 20)^2 + 0·00000001 \ (t - 20)^3$$

Cells made up with acid have a slightly lower E.M.F. The form of cell used at the N.P.L. is shown in Fig. 4 (XII *), and the specifications for the normal Weston cell are as follows : The electrolyte is a saturated solution of cadmium sulphate $3CdSO_4.8H_2O$, the electrolyte being neutral to Congo red. The cadmium sulphate is dissolved in hot water, cadmium oxide is added to make the solution basic, and 1 per cent of hydrogen peroxide is then added. After heating on a water-bath for 4 hours the solution is filtered. The filtrate is slightly acidified with sulphuric acid, evaporated to one-fourth its volume and filtered through a platinum cone in a glass funnel; the crystals in the funnel are washed twice with cold water, dissolved in a slight excess of water containing 1 in 10,000 sulphuric acid, filtered, and the solution set aside to crystallize. These crystals are also washed with cold water and are then air-dried. The powdered crystals are shaken either with distilled water or with 0·1 normal sulphuric acid according as the neutral or acid solution is to be prepared. The positive electrode is mercury which is purified in the following way : The mercury is placed in a large dish

FIG. 4 (XII *)

inside which is a small dish containing a small quantity of mercury. Platinum wire electrodes sealed into glass tubes make contact with the two portions of mercury, that in the smaller vessel being the cathode. An electrolyte, consisting of 90 parts water, 5 parts sulphuric acid, and 5 parts nitric acid, is poured in so as to cover the upper edge of the smaller vessel to a depth of 2 cm. A current of $\frac{1}{2}$ amp. is passed for 2 hours for each kilogram of mercury in the outer vessel. The residue in the outer vessel is then removed, washed, dried, and distilled *in vacuo.*
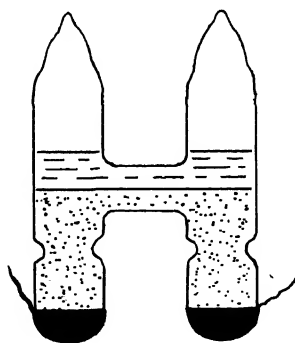
The negative electrode is an amalgam containing 10 per cent of cadmium. A small dish containing a weighed amount of mercury is placed in a larger dish. An electrolyte containing dilute slightly acid cadmium sulphate solution is poured to a depth of 2 cm. above the edge of the smaller vessel. The cathode is a platinum wire sealed in glass and placed in the mercury. The anode is a stick of cadmium wrapped in filter paper. A current of one-tenth of an ampere is passed for sufficient time to ensure that the cathode contains more than 10 per cent of its weight of cadmium. The alloy is removed, melted under dilute sulphuric acid (1 : 20), washed, dried, and weighed ; the calculated weight of mercury required to reduce the cadmium content to 10 per cent is added and the amalgam is again melted and stirred.

The depolarizer used at the anode is a paste made by adding mercurous sulphate to powdered cadmium sulphate and mixing into a paste with a saturated solution of cadmium sulphate.

The mercurous sulphate may be made by preparing mercurous nitrate by acting upon 200 grams of pure mercury with 30 ml. of concentrated nitric acid. When the reaction is complete the salt and the solution are added to 400 ml. of warm dilute nitric acid (1 : 40) ; the solution is filtered and run in a fine stream with constant stirring into 2 litres of hot dilute sulphuric acid (1 : 3) to which a little mercury has been added. If the sulphuric acid is diluted just before use it will be at a suitable temperature. The salt is washed three times by decantation with 0·1 N. sulphuric acid and then filtered. The residue is washed several times with the sulphuric acid and then with saturated cadmium sulphate solution similar to that to be used in making up the cell. If the acid electrolyte is to be used in the cell the mercurous sulphate is placed in a clean stoppered bottle together with powdered cadmium sulphate crystals, saturated cadmium sulphate solution, and a quantity of mercury equal to the amount of mercurous sulphate, and the contents of the bottle are well shaken. With the neutral electrolyte a thick paste is made and very violent shaking used to disseminate the mercury in small globules throughout the paste. To set up the cell the wires are first amalgamated by placing an acid solution of mercurous nitrate in the cell and with a platinum wire as anode passing a current to the two fused-in wires as cathodes. The cell is washed twice with dilute nitric acid, then with water, and is finally dried in the oven. One limb of the H vessel is placed in boiling water and the cadmium amalgam is melted by heating, and poured in to a sufficient depth to cover the platinum wire ; on cooling the amalgam solidifies. A sufficient amount of pure mercury is put into the other limb to cover the wire therein. Above the mercury is placed the depolarizer paste, then finely divided crystals of cadmium sulphate, and finally the solution. On the amalgam side is added cadmium sulphate crystals and then the saturated solution. When the cell has been filled the tops are sealed. The acid cell is reputed to give a very constant E.M.F., and if made up in the manner described this is about 62 microvolts below that of the neutral cell. Commercial cells are usually of the unsaturated type, i.e. they are made up with a solution which is saturated at 4° and is therefore unsaturated at the ordinary laboratory temperature ; the temperature coefficient of these cells is much lower than that of the saturated cell, being less than 0·00001

volt per degree. The E.M.F. of the unsaturated cell is not the same as. that of the normal cell, and its value is therefore determined experimentally and marked on the case.

The Indicator. When measurements are required of an accuracy a little better than 0·001 volt a capillary electrometer gives satisfactory results. A modified form of Ostwald's capillary electrometer is shown in Fig. 5 (XII *). The arms a and m each contain mercury, and this is connected to the binding posts e and f by means of the sealed-in platinum wires; the arms a and b are connected by the capillary c, and above m in the arm b is dilute sulphuric acid (1 : 6). When the mercury in a is charged positively and that in b nega- tively, the surface tension is decreased and the mercury will move up the tube. A cover-slip d sealed behind the meniscus makes its position more easily observable and this position is observed by means of a reading microscope with a horizontal cross-hair. Before using the electrometer it should be tilted several times to wet thoroughly the

FIG. 5 (XII *)

capillary tube. When not in use the terminals are short-circuited by the metal bar g; on depressing this bar contact of the bar with e is broken

FIG. 6 (XII *)

and with h and f made. The mercury in a should be con- nected to the positive terminal so as to prevent the formation of mercurous sulphate at the capillary surface. Fig. 6 (XII *) shows an Ostwald tube with a horizontal capil- lary c; if this is inclined so that the end of b is raised, the mercury in c will have to move a considerable distance along the tube to get a small increase in height. The same principle is used in Sand's elec-

trometer, shown in Fig. 7 (XII *), which is a sealed-in form with arrange- ments for moving the mercury and acid to different parts of the tube so that a fresh mercury surface can readily be obtained in the capillary. The
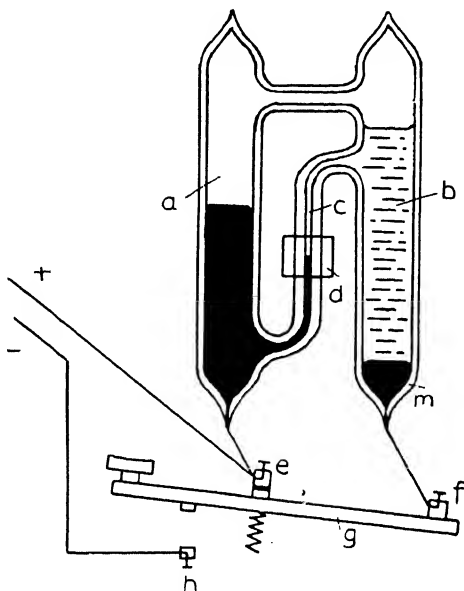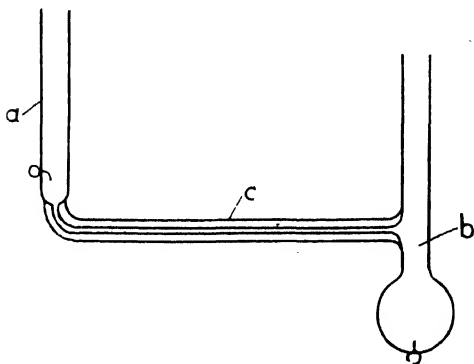
instrument is attached to a brass arm which is adjustable so that the slope of c can be varied. Below c a scale is fixed which is viewed through a small microscope ; with one of these instruments in good working order a sensitiveness of 0·0001 volt is attainable. For work of greater accuracy a galvanometer is used and the fact that it is to be used as a null point indicator should be borne in mind in selecting a suitable instrument for the purpose. The galvanometer is to be used to indicate small differences of
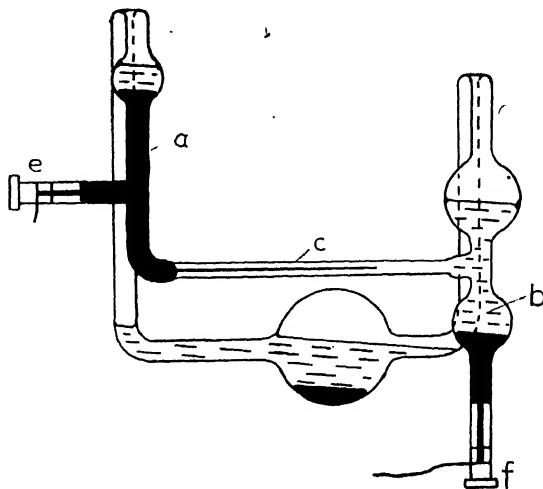

FIG. 7 (XII *)

potential so that its volt sensitivity would appear to be the factor which would be of importance in this connexion. The microvolt sensitivity usually means the deflection in millimetres produced on a scale at a distance of 1 metre when 1 microvolt is applied at the terminals of the galvanometer. The resistance of some of the cell chains used in series with the galvanometer may amount to 2,000 ohms, so that a microvolt applied to the terminals of cell chain plus galvanometer will give a very much smaller deflection.

The Megohm Sensitivity. This is the number of megohms of resistance which must be placed in series with the galvanometer in order that an impressed E.M.F. of 1 volt may cause a deflection of 1 mm. on a scale at 1 metre distance. This megohm sensitivity is the same numerically as the microampere sensitivity, the latter being the number of millimetres deflection caused by 1 microampere. It is this last sensitivity which is important in our case. With regard to the resistance of the galvanometer it is desirable that this should be of the same order as that of the cell to be measured.

The Setting of the Instrument. The final setting is facilitated if the galvanometer is damped. In the first part of the setting the key is tapped and the direction of the movement of the spot of light is sufficient to indicate the want of balance and its direction. Towards the end of the setting, when the movements become very small, the spot must be allowed to come

to rest before the key is tapped ; this is where the damping becomes necessary. If the terminals of the galvanometer are short-circuited through a resistance and a current is passed through the galvanometer, causing a deflection of the coil, as the coil moves back it will be moving in a strong magnetic field so that an induced current is set up and the direction of this will be such as to oppose the motion of the coil, whilst its magnitude will depend upon the resistance of the galvanometer coil and the damping coil together. The shunt-coil resistance can be adjusted to such a value that the coil will return to its zero position and stop there without oscillation ; this resistance is then called the critical damping resistance.

Example. As an illustration of suitable galvanometers the characteristics may be given of the Leeds and Northrup galvanometer, designed for H-ion work with their potentiometer, and of the instrument used by Clark :

	Coil resistance	Critical damping resistance	Period	Megohm sensitivity
L. & N.	1,000 ohms		3 secs.	40–50
Clark	510 ohms	1,000 ohms	5·4 secs.	1,973

Theory. When an electrode of a metal is immersed in a solution of a salt of the same metal a potential difference is set up between the metal and the solution ; in this case the electrode is said to be reversible because it is in contact with ions of its own kind. The value of the E.M.F. depends upon the concentration of the ions, so that a cell called a concentration cell can be set up. Thus, for example :

$$+$$

Silver	0·1 N.	0·01 N.	Silver
electrode	$AgNO_3$	$AgNO_3$	electrode
	C_2 B	C_1 C	
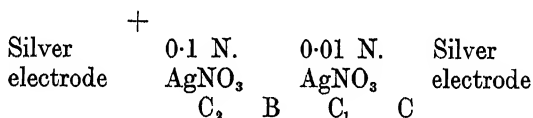
The E.M.F. of this cell is the sum of the E.M.F.s at A, B, and C due respectively to the metal — 0·1 N. $AgNO_3$ junction, the 0·1 N. $AgNO_3$ — 0·01 N. $AgNO_3$ junction, and the 0·01 N. $AgNO_3$ — metal junction. Neglecting the liquid-liquid P.D. the E.M.F. of the cell is given by

$$E = \frac{RT}{nF} \log_e \frac{C_2}{C_1}$$

where   R is the gas constant

T is the absolute temperature

n is the valency of the metal

F is the charge on 1 gram equivalent of the ion

C_1 and C_2 are the concentrations of the ions in the two half-elements of the cell.

R in volt coulombs is 8·32 and F is 96,540 coulombs, and multiplying by 2·303 to convert to ordinary logs we get

$$E = \frac{\cdot0001985}{n} T \log \frac{C_2}{C_1}$$

The liquid-liquid P.D. in a concentration cell is given by the equation

$$e_2 = \frac{v - u}{u + v} \frac{RT}{nF} . \log_e \frac{C_2}{C_1}$$

where v is the velocity of the anion

$\quad u$ „ „ „ kation.

In the case of silver nitrate v is greater than u.

$$\frac{u}{u + v} \quad \text{is the transport number of the kation.}$$

$$\frac{v}{u + v} \quad \text{is the transport number of the anion.}$$

In the cell shown diagrammatically above the Ag is positive to the deci-normal silver nitrate. The natural diffusion process at the liquid-liquid interface will cause the faster-moving NO_3' ion to pass more quickly to the dilute solution, which will thus be negatively charged with respect to the concentrated solution. So that if the P.D.s at A, B, and C are e_1, e_2, and e_3, the total E.M.F. of the cell will be

$$E = e_1 + e_2 - e_3$$

The complete expression for the $AgNO_3$ cell may also be written:

$$E = \frac{2v}{u + v} \frac{RT}{nF} \log_e \frac{C_2}{C_1}$$

If u were greater than v we should substitute $2u$ for $2v$ in the equation. In the case of silver nitrate the transport number of the NO_3' ion is 0·528, so that $\dfrac{2v}{u + v}$ is 1·056 and neglecting the liquid-liquid P.D. will introduce an error of 5·6 per cent. It has been shown that in this case the liquid-liquid P.D. can be eliminated by inserting a saturated solution of ammonium nitrate between the two half-elements of the cell.

Another method of eliminating the P.D. is to have an additional electro-lyte, e.g. KNO_3 or KCl, present in the same concentration in each half-element, and for this concentration to be much greater than that of any other electrolyte present; most of the current is then carried by this electro-lyte. The method is of limited application owing to reactions with the other electrolytes present and alteration in their degrees of dissociation.

Cohen measured the liquid-liquid P.D. with the following cells:

$$\text{Zn} \quad | \quad \text{ZnSO}_4 \; C_1 \quad | \quad \text{ZnSO}_4 \; C_2 \quad \text{Zn}$$
$$\pi$$

$$E_1 = \frac{RT}{2F} . \log_e \frac{C_2}{C_1} + \pi$$

Hg Hg_2SO_4 saturated Hg_2SO_4 saturated   Hg
$\quad$ $ZnSO_4 \; C_1$ $ZnSO_4 \; C_2$
$$\pi$$

$$E_2 = -\frac{RT}{2F} \log_e \frac{C_2}{C_1} + \pi.$$

therefore

$$E_1 + E_2 = 2\pi$$

'The following are the values of π in millivolts at 25° calculated from Henderson's formula [1]: the arrow shows the direction of the current in the solution.

HCl	KCl		KCl	KCl	
1.0 N	3.5 N	14.0	1.0 N	3.5 N	0.2
1.0	1.0	27.0	0.1	3.5	0.7
0.1	3.5	4.0	0.01	3.5	1.1
0.1	1.0	9.7	0.1	1.0	0.4
0.1	0.1	27.0			

$\frac{1}{2}H_2SO_4$	KCl		NaOH	KCl	π
0.1 N	3.5 N	4.0	0.1 N	3.5 N	2.0
0.1	1.0	9.0	0.1	1.0	6.0
0.1	0.1	30.0	0.1	0.1	20.0

NaCl	KCl	
0.1 N	3.5 N	0.2
0.1	1.0	0.9
0.1	0.1	4.6

'The values at 18° do not greatly differ from the above. The calculated values may be in error by several millivolts in the case of the strongly acid or alkaline solutions.'

Concentration cells can also be prepared with one solution, but with electrodes consisting of amalgams of different concentration, e.g. zinc in mercury of concentration C_1 and zinc in mercury of lower concentration C_2 dipping into a solution of zinc sulphate; here

$$E = \frac{RT}{nF} \log_e \frac{C_1}{C_2}$$

Non-metals can be used in concentration cells, as for example in the case of the hydrogen electrode. In these cells, hydrogen gas bubbles through the liquid on to a platinum electrode which itself is inert but which supplies the necessary mechanical rigidity to the gas. Such a cell would be:

Platinum electrode   HCl C_1 HCl C_2 Platinum electrode
   in H_2 gas   in H_2 gas

Since the E.M.F. of a cell is made up of at least two parts, one corresponding to each electrode, for purposes of comparison it is necessary to have standard electrodes which are reproducible readily and which give a constant E.M.F. in order that these may be used to build up one-half of the cell. For this purpose the calomel and the hydrogen electrodes are very largely used. The calomel electrode is made up of mercury in contact with mercurous chloride (mixed with mercury to prevent the presence of mercuric chloride), and in contact with this is potassium chloride solution saturated with mercurous chloride. If the potassium chloride is present in normal solution, the electrode is a 'normal calomel electrode'; if the potassium chloride is N/10, the electrode is a 'decinormal calomel electrode'.

'The absolute values of the E.M.F. are:

|	18°	25°
Saturated calomel electrode .	0.5252 volt	0.5266 volt
Normal calomel electrode .	0.5600 ,,	0.5648 ,,
Decinormal calomel electrode	0.6130 ,,	0.6185 ,,

[1] *Zeits. f. physik. Chem.*, 59, 118, and 63, 325.

'The temperature coefficients are :

Saturated electrode	. . .	+ 0·00020	volt per degree
Normal electrode	. . .	+ 0·00068	,, ,, ,,
Decinormal electrode	. . .	+ 0·00079	,, ,, ,,

These electrodes are used as standards in most cases.'

The hydrogen gas (at atmospheric pressure) electrode in contact with HCl solution, in which the H-ion (not total acid) concentration is normal, is also used as a standard. If we set up the cell

$$\text{Hg} \mid \text{Hg}_2\text{Cl}_2 \mid \text{N.KCl.} \mid \text{N.H}^{\cdot} \text{ in HCl.} \mid \text{H}_2$$
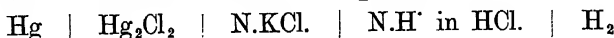
we find that the E.M.F. is 0·2828 volt, the mercury being positive to the gas.

'The normal hydrogen electrode is now generally taken as the standard for reference purposes and its E.M.F. is taken arbitrarily as zero at all temperatures. On this basis the E.M.F. of the N calomel electrode becomes + 0·2828 volt, and since we know its absolute value to be + 0·5600 volt we can convert an experimental value determined with the normal hydrogen electrode taken as zero to the absolute value by the addition of 0·2772 volt and vice versa.

'So we get, with the normal hydrogen electrode as zero, the E.M.F.s of the calomel electrodes at 18°.

Saturated calomel .	+ 0·2480 volt
Normal calomel .	+ 0·2828 volt
Decinormal calomel.	+ 0·3358 volt'

The E.M.F. of the hydrogen gas electrode is affected by the pressure of the gas, a decreased pressure giving a low value for the E.M.F. The correction to be applied is given by the equation

$$E = \frac{RT}{2F} \log_e \frac{1}{P_{H_2}}$$

where P_{H_2} is the pressure of the hydrogen gas in atmospheres, i.e. the corrected barometric pressure minus the aqueous vapour pressure and plus any back pressure in the apparatus.

Since we are unable to prepare a solution of HCl which we know to be exactly normal with reference to hydrogen-ion concentration, we are compelled to obtain our normal electrode by comparison with a calomel electrode with which it will show an E.M.F. of 0·2828 volt.

According to the newer view-point of Bjerrum, Bronsted, and others, the normal cell should be one in which the hydrogen ions have an 'activity' rather than a 'concentration' equal to 1.

Preparation of the Calomel Electrode. The preparation of pure mercury has been described in connexion with the Weston cell. Pure calomel is prepared by redistilling pure nitric acid and using this to dissolve some of the purified mercury (which must be in excess). Throw this solution into a large excess of water distinctly acidified with nitric acid and to this solution slowly add dilute hydrochloric acid prepared by distillation of pure 20 per cent acid, neglecting the first and last portions of the distillate. Add a little mercury and wash repeatedly with pure distilled water. Calomel can also be prepared by the electrolysis of HCl solution with a platinum

cathode and a mercury anode, using a current from two accumulators. The mass of the mercury at the bottom of the vessel and also its surface are continually stirred by rotating paddles. Before making up the cell the calomel, always with a little mercury, is shaken repeatedly with the potassium chloride solution to be used in making up the cell. Different forms of electrode vessel are shown in Figs. 8 (XII *) and 9 (XII *), and at *a* in Fig. 13 (XII *), and at *a* and *b* in Fig. 14 (XII *). In Fig. 8 (XII *) a contact is supplied leading out of the thermostat, and there is a three-way stopcock for flushing out potassium chloride solution, which has become contaminated by diffusion from the liquid in the middle vessel. Fig. 9 (XII *) shows a saturated calomel electrode for use in titrations; fresh potassium chloride enters the cell from the U-tube where it has taken on the temperature of the bath and become saturated with calomel, a layer of this being placed in the bend of the U-tube. The electrode in Fig. 14 (XII *) is a closed electrode in which the potassium chloride is
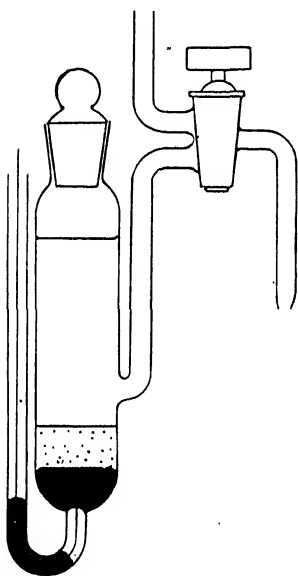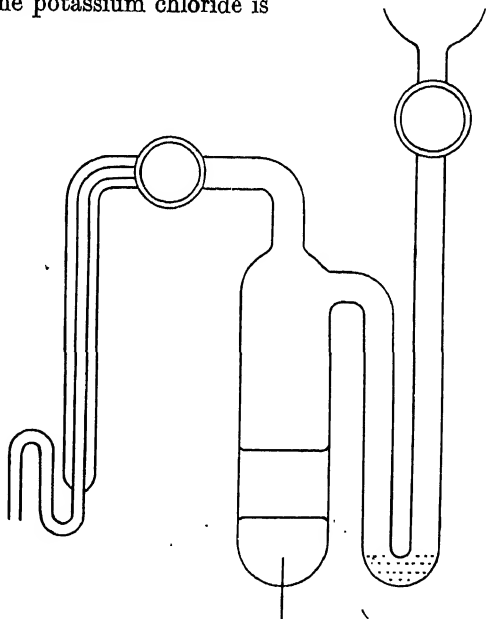

FIG. 8 (XII *)   FIG. 9 (XII *)

saturated; such electrodes do not require such careful protection from contamination and the use of saturated potassium chloride solution reduces the total resistance of the cell. The electrode *a* is used as a working standard only, the actual standards being the normal or decinormal electrodes *b*.

Hydrogen Electrodes. The platinum used to support the hydrogen is either in the form of foil or wire or of a thin film deposited on glass. A foil electrode is made by welding a short piece of wire to the foil by hitting with a small hammer on a hard surface while the foil is heated with a blast-

lamp, drawing a glass tube to a blunt point and sealing in the wire so that the glass extends down on to the foil to hold it stiff. A film electrode can be made by sealing a thin platinum wire into the end of a hard glass tube and breaking off the projecting piece of wire flush with the surface. The tube is then heated and a solution of chloroplatinic acid and glycerine is applied with an asbestos swab. The temperature of the glass should be high enough to burn off the glycerine at once and leave a film of platinum black on the surface of the glass ; this film is made adherent by heating the glass strongly. A piece of glass is sealed on to cover the projecting platinum point. A deposit of platinum (or iridium or palladium) black on the electrode is obtained by electrolysis of a 2 per cent solution of platinic chloride in HCl ; a current from two storage cells is used so as to produce a vigorous
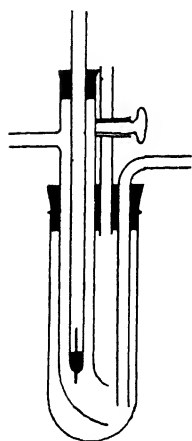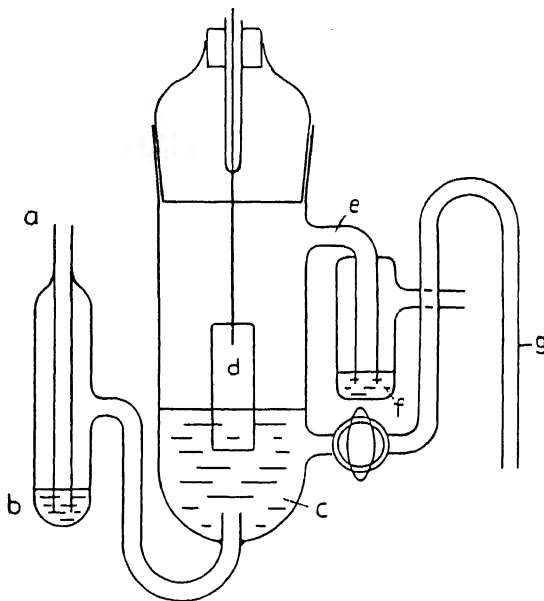

FIG. 10 (XII *)   FIG. 11 (XII *)

evolution of gas ; electrolysis is continued for a few minutes until a thin film is produced which just covers the platinum. The use of lead acetate is not recommended ; if the deposit does not come down readily a little formic acid is added. Immediately after the deposition of the platinum the electrode is transferred to dilute sulphuric acid and is saturated with hydrogen. The film may be tested for adherence by holding under a stream of water.

Examples of different types of hydrogen electrode vessels are shown in Figs. 10 (XII *) to 14 (XII *). In Fig. 11 (XII *) the hydrogen enters at *a* and passes through the solution in *b* so that the gas becomes saturated with vapour at the temperature of the bath before entering the solution *c* in the electrode chamber. The gas next passes over the electrode and out through the tube *e* ; the bent tube *g* serves to make contact with the solution in *c* and the connecting vessel. Fig. 12 (XII *) is a tube designed

by McClendon and Magoon [1] for use with small quantities of material (in this case—blood). Fig. 10 (XII *) shows an electrode for use in titrations, in which a rapid stream of gas passes down the tube containing the electrode, so protecting it from oxygen.[2] Clark's vessel,[3] designed for use in biological determinations, is an example of a type which can be shaken. Fig. 14 (XII *) shows this electrode vessel attached to the frame which
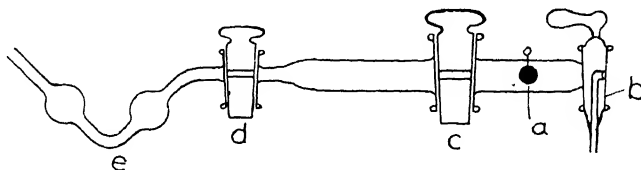

FIG. 12 (XII *)

rocks on the eccentric m. The rocking brings every part of the solution in contact with the electrode d.

Figs. 13 (XII *) and 14 (XII *) show examples of complete cells, the so-called gas chains used for measurement of hydrogen-ion concentration. In Fig. 13 (XII *), a is the calomel electrode and b the hydrogen electrode, while c is the connecting vessel containing saturated potassium chloride
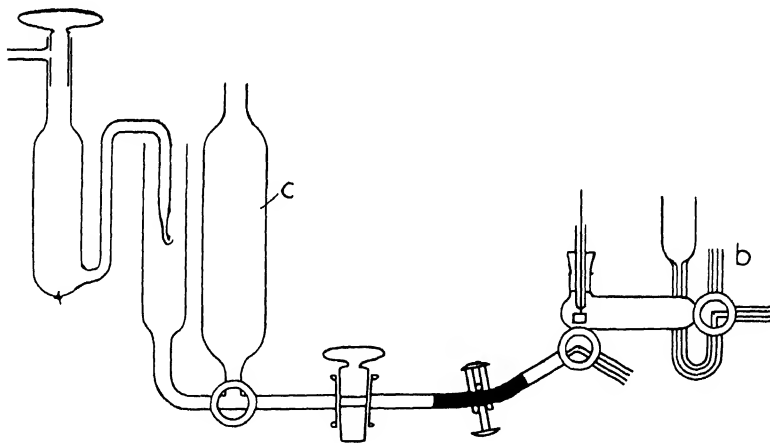

FIG. 13 (XII *)

solution. The apparatus in Fig. 14 (XII *) is designed for use in an air-bath and with rocking electrodes, and it will be noticed that the use of the electrode a enables us to have no closed taps between the two electrodes. To use this apparatus to measure the hydrogen ion concentration of a solution, we proceed in the following way. It will be remembered that a is a saturated-calomel electrode and bb are tenth-normal electrodes. The gas electrode chamber x is filled with distilled water from k and this is displaced by purified hydrogen from w admitted through the tap g. The

[1] *J. Biol. Chem.*, 1916, *25*, 669.   [2] Bunker, *J. Biol. Chem.*, 1920, *32*, 11.
[3] *J. Biol. Chem.*, 1915, *27*, 475.

chamber is washed out thoroughly with hydrogen by allowing it to enter under pressure from w and then to fall to atmospheric pressure by connecting to the tube o by means of the tap g. The solution to be measured is now placed in k and the vessel x is washed out several times with this, displacing it through the tap e into the tube c by means of hydrogen entering through tap g. The vessel is next tilted down to its lowest position and solution is run in so that it merely touches the bottom of the electrode d and hydrogen is admitted at atmospheric pressure. The tube is rocked to get it into equilibrium and as it rocks the electrode d is alternately completely exposed to solution and then to gas. Saturated potassium chloride is contained in t and tenth-normal potassium chloride saturated with calomel in s. By means of taps p and e saturated potassium chloride from t can be caused to fill the tubes of the connecting vessel from p up to c. The first step is to measure the E.M.F. of the saturated electrode a against the battery
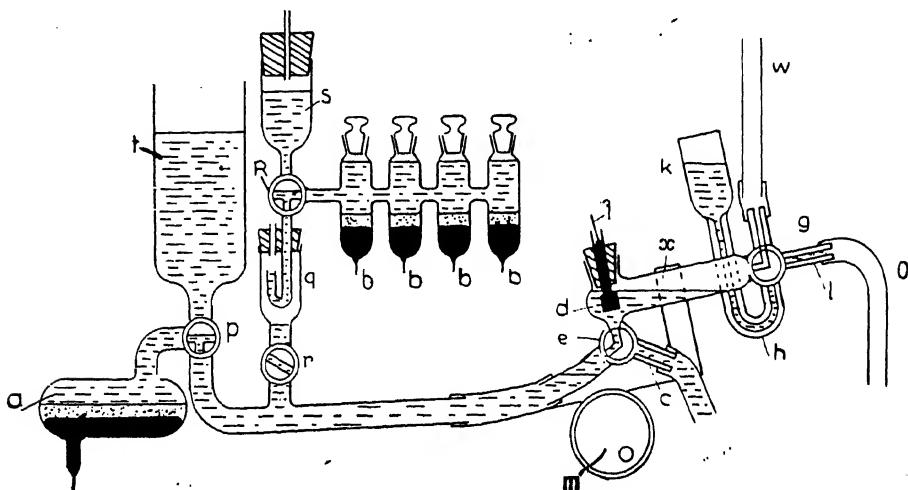

FIG. 14 (XII *)

of standard electrodes b. Connexion between the two is obtained by turning the tap R to allow tenth-normal KCl to flow from s into q. With tap e closed and taps p and r open and R connecting b and q, the E.M.F. of a against each of the electrodes b is measured. Tap R is closed and with r and e open the solution in q is run out. With r closed the connecting tubes can then be flushed out with saturated KCl from t. The E.M.F. between a and f is next to be determined. The rubber tube connecting the two parts of the apparatus is pinched with tap e connected to c. This tap is then turned to connect to x and the pressure on the rubber is released so that some of the solution from x is drawn down into the tube and makes a broad junction with the KCl solution. The hydrogen pressure is once more adjusted to atmospheric (and this pressure is read) and the E.M.F. measurement can be commenced and continued until a steady value is attained.

Preparation of Hydrogen. With regard to the hydrogen used, compressed hydrogen from a cylinder can be purified by passing through

a solution of alkaline pyrogallol and then should be bubbled through some of the solution under measurement, if a bubbling electrode is used, so that the concentration of the solution will not be altered. A special hydrogen generator used by Clark is shown in Fig. 15 (XII *). The cover of the museum jar is drilled with a metal tube fed with carborundum and glycerine or a solution of camphor in turpentine. It contains a 10 per cent solution of caustic soda and nickel electrodes are used. The hydrogen passes through the tap *e* into the tube *b*, which contains concentrated sulphuric acid, which dries it and removes spray; it then passes through the tungsten-filament lamp *c*, where traces of oxygen are burnt out, to the tube *d*. About 4·5 amps. are used to produce a rapid stream of gas and this is reduced to produce a slow stream by throwing the lamp L into series by means of the switch S. Switch *g* controls the filament of the lamp *c*.
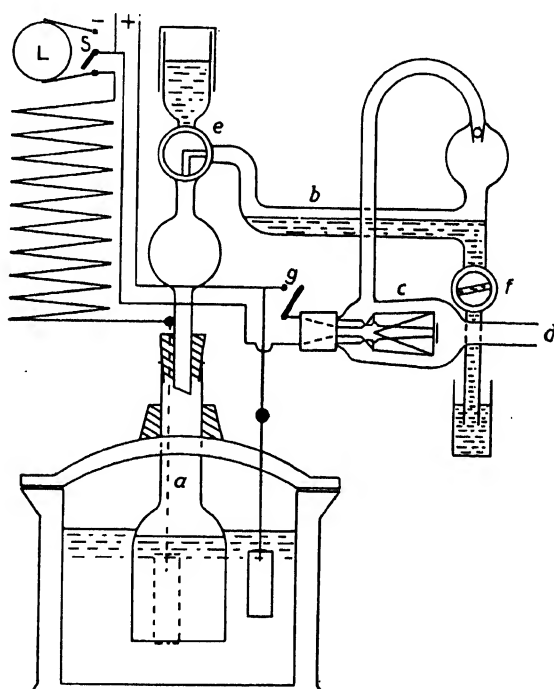

· FIG. 15 (XII *)

In making E.M.F. measurements electrical shielding should always receive careful consideration. The principle of the method is that the whole of the apparatus should stand upon a large earthed metal plate with which all parts of it should be in good metallic connexion.

Electrical leaks are very difficult to prevent in water-baths, so that air thermostats are more satisfactory for E.M.F. measurements.

Example. As an example of a concentration cell the following may be constructed :

$$\text{Ag} \quad 0.02 \text{ N.AgNO}_3 \quad | \quad 0.002 \text{ N.AgNO}_3 \quad | \quad \text{Ag}$$
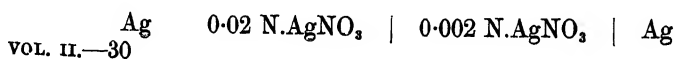
Here the E.M.F. can be calculated from the equation

$$E \qquad \frac{2v}{v} \cdot \frac{RT}{nF} \times \log_e \frac{C_1}{C_2}$$

The transport number of the anion is $\dfrac{v}{u + v} = 0 \cdot 528$, and taking T as 18°

$$\therefore E = 2 \times 0 \cdot 528 \times 0 \cdot 058 \log \frac{C_1}{C_2}$$

$0 \cdot 02$ N.AgNO$_3$ is 91 per cent dissociated, hence the ionic concentration of Ag $= 0 \cdot 02 \times 0 \cdot 91$.

$0 \cdot 002$ N.AgNO$_3$ is 93 per cent dissociated, so that $C_2 = 0 \cdot 002 \times 0 \cdot 93$

$$\therefore E = 1 \cdot 056 \times 0 \cdot 058 \log_{10} \frac{0 \cdot 0182}{0 \cdot 00186}$$

$$= 1 \cdot 056 \times 0 \cdot 058 \times \log_{10} 9 \cdot 784$$
$$= 1 \cdot 056 \times 0 \cdot 058 \times 0 \cdot 9905$$
$$= 0 \cdot 0607 \text{ volt}$$

The Silver Electrodes. These are prepared by passing pieces of silver wire through glass tubes and fastening them therein by means of sealing-wax. The projecting ends are then plated with silver. A solution of silver nitrate containing 3·5 grams per litre is treated with dilute potassium cyanide with constant stirring until the first formed precipitate of silver cyanide is redissolved. Using a piece of silver foil as anode and the silver wires as cathodes a current of 0·2 milliamp. is passed until the surface of the wires is covered with the electrolytic deposit.

Vessels similar to that shown in Fig. 16 (XII *) are used, one being filled with 0·02 N. silver nitrate, and the other with the more dilute solution. When the electrodes have been put in, the ends of the inverted U-tubes are put into a beaker containing normal potassium nitrate and contact made by blowing at the side-tubes. The E.M.F. is then measured and compared with that calculated. Alternatively the two halves of the cell may be combined in turn with a calomel electrode, and the difference of the E.M.F.s of the two cells so obtained be used to compare with the calculated E.M.F. Similar experiments may be carried out with zinc in zinc sulphate or copper in copper sulphate. Zinc electrodes of pure zinc are rubbed with dilute sulphuric acid, and then amalgamated with pure mercury. Copper electrodes are formed of wire sealed in glass tubes with sealing-wax and plated with copper, using a current of 1 to 2 milliamps. and a plating solution containing

    1,000 ml. water
      150 grams of recrystallized copper sulphate crystals
       50 ml. conc. sulphuric acid
       50 ml. alcohol

A concentration cell, in which the concentration of the electrodes is different while the concentration of the solutions is the same, can be prepared with zinc amalgams.

A large potential vessel similar to that shown in Fig. 16 (XII *) is used and in this is placed an accurately weighed quantity of pure mercury, say 70 grams. A stirrer passes through the rubber stopper and also a rod of pure zinc; the electrolyte is normal zinc sulphate. The amalgam is prepared by connecting a platinum-wire electrode with the mercury, and to this the negative terminal of a 4-volt battery; the positive terminal is connected to the zinc rod through a standardized milliammeter, a variable rheostat, and a key. The rheostat is set to give a current of 8 to 10 milliamps., the time being taken by a stop-watch, and the current being maintained and kept steady for a period of 10 minutes.
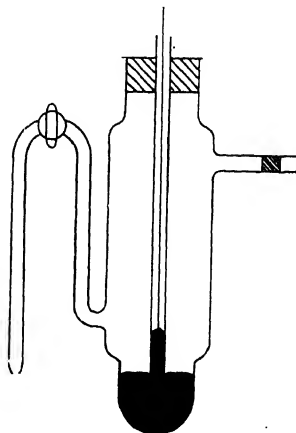
FIG. 16 (XII *)

The weight of zinc set free at the cathode is given by eCt, where e is the electrochemical equivalent of zinc, i.e. 0·00338, C is the current in amperes, and t the time in seconds. The concentration of the amalgam in gram molecules per litre is

$$\frac{W \times 1,000}{v \times 65}$$

where W is the weight of zinc, v is the volume of the mercury, and 65 is the molecular weight of the zinc; e.g. if the current were 8 milliamps and were passed for 10 minutes, and 70 grams of mercury were used, the concentration would be obtained thus:

$$W = 0 \cdot 00338 \times 0 \cdot 008 \times 600$$

$$C = \frac{0 \cdot 00338 \times 0 \cdot 008 \times 600 \times 1,000 \times 13 \cdot 59}{70 \times 65}$$

$$= 0 \cdot 0485$$

When the amalgam has been thoroughly stirred, the cell is made up with a calomel electrode and a middle vessel containing saturated potassium chloride, and the E.M.F. is measured. The tap of the connecting tube is not greased, but is wetted with the zinc sulphate solution. A more concentrated amalgam is now prepared by continuing the passage of the current for a further period of 30 minutes. If the current is maintained at the same value as before, the total time is now 40 minutes and the concentration of the amalgam is 0·194 gram molecule per litre.

The E.M.F. of the new amalgam electrode with the calomel electrode is now measured, and if the difference of the two E.M.F.s is denoted by E, the experimental value of E obtained can be compared with that calculated for the equation

$$E = \frac{0 \cdot 058}{n} \log_{10} \frac{C_1}{C_2}$$

The following results have been obtained with zinc amalgams:

t°	C_1	C_2	E observed	E calculated
11·6	0·003366	0·00011305	0·0419 volt	0·0416
18·0	0·003366	0·00011305	0·0433 ,,	0·0425
12·4	0·002280	0·0000608	0·0474 ,,	0·0445
60·0	0·002280	0·0000608	0·0520 ,,	0·0519

Determination of Hydrogen Ion Concentration of a Solution. A cell is set up with the solution in question in contact with the hydrogen electrode and this is combined with, for example, a normal calomel electrode. The E.M.F. is measured from calomel to hydrogen. As an example, take the case of 0·01 N.HCl solution in which the measured E.M.F. was $+ 0·4123$ at 18°. The barometric pressure (at 18°) was 754 mm. and this, when corrected down to 0°, becomes 751·7 mm. The water vapour pressure at 18° is 15·5 mm. so that the partial pressure of the hydrogen gas (assuming no back pressure) becomes 736·2 mm.

The correction to be applied to the observed E.M.F. for this low pressure is given by

$$E = \frac{0·0001984 \times 291}{2} \times \log \frac{760}{736·2}$$
$$= + 0·0004 \text{ volt}$$

Therefore the corrected E.M.F. of the chain becomes $+ 0·4127$ volt.

The chain is $Hg.Hg_2Cl_2 \mid N.KCl \mid\mid 0·01 \ N.HCl \mid H_2$ and the total E.M.F. is E where

$$E = e_1 + e_2 - e_3$$

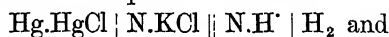where e_1 is the electrode potential of the calomel electrode

e_2 is the junction E.M.F. and is equal to 0·0097 volt

e_3 is the electrode potential of the $HCl.H_2$

hence $0·4127 = e_1 + 0·0097 - e_3$

$0·4030 = e_1 - e_3$

now the normal calomel electrode against the normal hydrogen electrode (as zero) gives an E.M.F. E' equal to 0·2828 volt. Here the chain is

$$Hg.HgCl \mid N.KCl \mid\mid N.H^{\cdot} \mid H_2 \text{ and}$$
$$E' = e_1 - e_4$$
$$\therefore + 0·2828 = e_1 - e_4$$
$$\text{but} + 0·4030 = e_1 - e_3$$
$$\therefore + 0·1202 = e_4 - e_3$$

i.e. the E.M.F. of the normal hydrogen electrode against our experimental hydrogen electrode is $+ 0·1202$ volt.

$$E = \frac{RT}{nF} \ln \frac{C_1}{C_2}$$

$$0·1202 = 0·0001984 \times 291 \log \frac{1}{C_2}$$

$$p\text{H} = \log \frac{1}{C_2} = \frac{0·1202}{0·0577} = 2·082$$

$$= \log 120·8$$

$$\frac{1}{C_2} = 120·8$$

$$C_2 = 0·00828$$

It will be noted that in the calculation, e_1, the potential of the calomel electrode, cancels out, so that it is unnecessary to know the absolute value of this : this is important because the absolute value cannot be determined with the same degree of accuracy as the relative values to other electrodes.

Determination of the Degree of Ionization of Water at 18°. Two hydrogen electrodes are required, and a cell is set up with dilute acid and alkali thus :

$$\text{H}_2 \mid 0\cdot01 \text{ N . HCl} \mid 0\cdot01 \text{ N . KCl} \mid 0\cdot01 \text{ N . KOH} \mid \text{H}_2$$
$$e_1 e_2 e_3 e_4$$
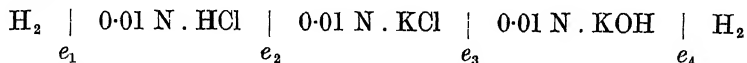
and the E.M.F. of the cell is measured ; let the value found be E_1.

This E.M.F. is made up of four potential differences :

e_1, dependent on the concentration of the hydrogen ions in the 0·01 N. HCl

e_2, the contact potential between 0·01 N. HCl and 0·01 N. KCl

e_3, the contact potential between 0·01 N. KCl and 0·01 N. KOH

e_4, dependent on the hydrogen ion concentration in the 0·01 N. KOH

e_2 and e_3 can be calculated from the mobilities of the ions by the equations

$$e_2 = 0\cdot058 \log_{10} \cdot \frac{u_1 + v_1}{u_2 + v_1}$$

$$e_3 = 0\cdot058 \log_{10} \frac{v_2 + u_2}{v_1 + u_2}$$

The mobilities of the ions concerned at 18° in 0·01 N. solution are

$$\text{H}^{\cdot} u_1 = 318$$
$$\text{K}^{\cdot} u_2 = 65\cdot3$$
$$\text{Cl}' v_1 = 65\cdot9$$
$$\text{OH}' v_2 = 174$$

so that the calculated values of e_2 and e_3 are

$$e_2 = 0\cdot0271 \text{ volt}$$
$$e_3 = 0\cdot0151 ,,$$

These two E.M.F.s act against the electrode potentials. The electrode potential E is equal to

$$0\cdot058 \log_{10} \frac{c_1}{c_2}$$

where c_1 is the concentration of hydrogen ions in the acid and c_2 that in the alkali, and $E = E_1 + 0\cdot0271 + 0\cdot0151$, where E_1 is the measured E.M.F.

Hence $\dfrac{C_1}{C_2}$ can be found.

The dissociation fractions of 0·01 N. solutions of HCl and KOH are 0·98 and 0·97.

Hence $C_1 = 0\cdot01 \times 0\cdot98 = 0\cdot0098$, so that C_2 can be calculated.

The concentration of the OH' ions in the caustic potash is
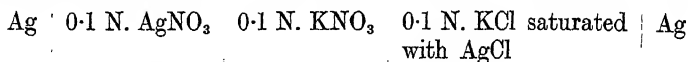
$$\text{C}_{\text{OH}} = 0\cdot01 \times 0\cdot97 = 0\cdot0097$$

so that in the potash solution

 C_2 is the calculated H· ion concentration

 $\text{C}_{\text{OH}'}$ is 0·0097

Hence the product $C_2 \times 0\cdot0097 = \text{K}$ can be calculated.

Measurement of the Solubility of Silver Chloride. The cell

$$\text{Ag} \mid 0{\cdot}1 \text{ N. AgNO}_3 \mid 0{\cdot}1 \text{ N. KNO}_3 \mid 0{\cdot}1 \text{ N. KCl saturated} \mid \text{Ag}$$
$$\text{with AgCl}$$

is set up and its E.M.F. measured. The preparation of the silver electrodes has already been described ; the addition of a drop of silver nitrate to the 0·1 N. KCl is sufficient to saturate the solution with silver chloride.

Then
$$E = \frac{2v}{u+v} \times 0{\cdot}058 \times \log_{10} \frac{C_1}{C_2}$$

where E is the measured E.M.F.,

$\dfrac{}{u+v}$ is the transport number of the $\text{NO}_3{'}$ ion,

C_1 the concentration of the Ag ion in the 0·1 N. AgNO_3 and C_2 that of the Ag ion in the AgCl solution.

$\dfrac{v}{u+v} = 0{\cdot}528$, and since 0·1 N. AgNO_3 is 81 per cent dissociated

$C_1 = 0{\cdot}081$ so that $E = 1{\cdot}056 \times 0{\cdot}058 \log_{10} \dfrac{0{\cdot}081}{C}$

which enables us to calculate the value of C_2. The concentration of the chloride ion in the AgCl element is practically that due to the 0·1 N. KCl, and since there is 85 per cent dissociated, $C_{Cl'} = 0{\cdot}085$. The solubility product S therefore equals $0{\cdot}085 \times C_2$, and S being known, the solubility of the silver chloride is $\sqrt{S}$ gram molecules per litre.

For example, the E.M.F. of such a cell at 25° was found to be 0·45 volt. N/10 AgNO_3 is 82 per cent dissociated at this temperature (from conductivity measurements).

Then $E = \dfrac{2v}{u+v} \times 0{\cdot}0002 \text{ T} \log_{10} \dfrac{C_1}{C_2}$

$0{\cdot}45 = 2 \times 0{\cdot}528 \times 0{\cdot}0002 \times 298 \log_{10} \dfrac{C_1}{C_2}$

$\therefore \log_{10} \dfrac{C_1}{C_2} = 7{\cdot}15$

$\therefore \dfrac{C_1}{C_2} = 1{\cdot}41 \times 10^7$

$C_1 = 0{\cdot}082$

$\therefore C_2 = \dfrac{0{\cdot}082}{1{\cdot}41 \times 10^7} = 5{\cdot}82 \times 10^{-9}$ gram molecules per litre

$\therefore C_{Ag.} \times C_{Cl'} = 5{\cdot}82 \times 10^{-9} \times 0{\cdot}085$

$\qquad = S = 4{\cdot}95 \times 10^{-10}$

$\therefore \sqrt{S} = 2{\cdot}2 \times 10^{-5}$ gram molecules of silver chloride per litre.

The Determination of Activities. An examination of the thermodynamic properties of solutions of strong electrolytes has led to the

introduction of the term 'activity' of the various components of the solution, to represent the effective concentration which is to be introduced into the Mass Action Law equation in place of the real concentration. Activities are not to be looked upon as empirical quantities to be put into equations instead of the concentrations in order to get agreement with experimental results. They are real quantities, namely the partial free energies of the substances in solution. In all cases the activities approach proportionality to the concentrations in very dilute solutions.

If F be the free energy change when 1 gram molecule is transferred from a solution of concentration c to a solution of concentration c_0,

for an ideal solution $F = RT \ln c/c_0$, and
for a real solution $F = RT \ln a/a_0$

where a/a_0 is the ratio of the activities of the two solutions.

If the second solution be the one selected as standard, usually the solution at infinite dilution, we may define its activity as being equal to its concentration, and $a_0 = c_0$. Then a/c is a measure of the deviation of the first solution from an ideal solution and a/c is called the activity coefficient γ.

Activities may be determined in various ways, e.g. from the vapour pressure of the solute, from distribution ratios, from the vapour pressure of the solvent and from E.M.F. measurements.

In the equation, $F_2 - F_1 = RT \ln\dfrac{a_+{}''.a_-{}''}{a_+{}'.a_-{}'} = 2RT \ln\dfrac{a_\pm{}''}{a_\pm{}'}$.

and $F_2 - F_1 = -$ NEF of the concentration cell, if we are working with a uni-univalent electrolyte and neglect the liquid-liquid junction.

If E_0 is the E.M.F. in the standard state (i.e. $a_\pm{}° = 1$) we have

$$- (E - E_o) = \frac{2RT}{NF} \ln a_\pm - \frac{2RT}{NF} \ln a_\pm$$

$$= 0.1183 \log a_\pm \qquad \frac{2RT}{NF} \ln 1 \text{ (at 25°)}$$

$$= 0.1183 \log a_\pm$$
$$= 0.1183 \log \gamma c \qquad\qquad \text{since } \gamma = a_\pm/c$$
$$= 0.1183 \log c + 0.1183 \log \gamma$$

therefore $E_0 - (E + 0.1183 \log c) = 0.1183 \log \gamma$.   .   (1)

and $E_0 - E_1 \qquad\qquad = 0.1183 \log \gamma$.

When $\gamma = 1$, i.e. when $c = 0$, E_0 is equal to E_1 : therefore to find the value of E_0 plot the values of E_1 (i.e. $E + 0.1183 \log c$) against c and extrapolate to zero concentration. Then by substitution in equation (1) calculate values of $\log \gamma$ and so γ at the various concentrations.

An example of the calculation is given from the results of Linhart [1] for the activity of hydrochloric acid from the cell $H_2 \mid$ HCl solution $\mid$ AgCl $\mid$ Ag.

[1] *J. Chem. Soc.*, 1919, 1178.

C_{HCl}	E corr. to 1 atm. H_2 pressure	E_1	γ
0·04826	0·3874	0·2317	0·8507
0·00965	0·4658	0·2274	0·9256
0·004826	0·5002	0·2262	0·9475
0·001000	0·5971	0·2242	0·9845
0·000483	0·6161	0·2238	0·9920
0·000242	0·6514	0·2236	0·9960

Calculation of column 3.

$$E_1 = E + 0\cdot1183 \log c$$
$$= 0\cdot3874 + 0\cdot1183 \times \log 0\cdot04826$$
$$= 0\cdot3874 + - 0\cdot1557$$
$$= 0\cdot2317 \text{ volts}$$

Plotting E_1 against c gives $E_0 = 0\cdot2234$ volt.

Calculation of column 4.

$$0\cdot1183 \log \gamma = E_0 - (E + 0\cdot1183 \log c)$$
$$= E_0 - E_1$$
$$= 0\cdot2234 - 0\cdot2317$$
$$= - 0\cdot0083$$

therefore $$\log \gamma = - 0\cdot0702$$
$$= \bar{1}\cdot9298$$
and $$\gamma = 0\cdot8507$$

The Glass Electrode. Haber and Klemensiewicz [1] found that a thin glass bulb filled with KCl solution into which dips a platinum wire, could be used as an electrode. The potential appears to depend partly upon the hydrogen-ion concentration and partly upon the concentration of the ions which the glass contains, such as sodium, calcium, &c.

If the concentration of the ions of the latter were constant the cell could be used for the measurement of hydrogen-ion concentration : while if the former were constant it might have applications where a metal electrode cannot be used, as with calcium, barium, &c.

One of the difficulties in the use of such cells lies in the very high resistance which is introduced into the chain : on this account Haber used a quadrant electrometer for the measurement of the potential.

MacInnes and Dole [2] have devised a glass electrode having a comparatively low resistance. They found that the best of the glasses tested had the composition, silica 72, soda 22, and lime 6 per cent. They prepared the electrodes in the following way : a piece of the glass weighing about 50 mg. was first melted into the end of a pyrex tube of about 4 mm. diameter. The glass was then heated to a low red heat and blown into the form of a bubble thin enough to show interference colours. A second tube, also about 4 mm. in diameter and of ordinary soft glass, was then heated to somewhat below red heat and was brought in contact with the bubble. This then fused on to the end of the glass tube and formed a thin flat dia-

[1] *Zeits. physik. Chem.*, 1909, *67*, 385.   [2] *J. Amer. Chem. Soc.*, 1930, *52*, 29.

phragm which was strong enough to support the pressure due to 9 cm. of mercury for a period of 3 weeks. The upper part of the electrode was covered with paraffin wax inside and out. This membrane had an initial resistance of 12 megohms falling to 8 on the second day : with decinormal sodium hydroxide it gave an initial error of -32 millivolts which did not alter with time, a very great advantage.

Measurement of the Activity of Hydrochloric Acid at 25° at Various Dilutions. Prepare the following solutions of hydrochloric acid, using pure 20 per cent acid which has been redistilled and the middle fraction only retained : N/20, N/100, N/200, N/1,000, N/2,000, N/4,000, and set up the cell

$$H_2 \mid x N. \; HCl \; solution \mid AgCl \mid Ag$$
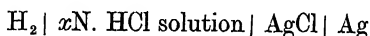
The silver electrode is prepared in the usual way and dips into a vessel containing some of the acid solution to which sufficient silver nitrate has been added to form a permanent precipitate ; the side arm of the hydrogen gas electrode also dips into the same solution.

Measure the E.M.F. of the cell with each of the acid solutions in turn and then proceed as in the example given above.

MacInnes and Dole made their measurements with a potentiometer using a Compton electrometer as a null instrument ; some care in screening was necessary and the leads were covered with a lead sheath, the cell was surrounded by a wire cage and the switches and key were placed in a tin box ; all screens were grounded. They found that the potential at the surface of the glass changes quantitatively with the hydrogen-ion concentration up to a pH value of 9·5, but that this limit is somewhat lowered in concentrated salt solutions. Fosbinder [1] describes a vacuum tube potentiometer for use in measurement of the E.M.F. of cells such as this, in which the resistance is very high.

ANTIMONY ELECTRODE

By far the most rugged of the various measuring electrodes, the antimony electrode is suitable for pH measurements in industrial processes over the range of 2 to 13 pH. Its low resistance enables it to be used with ordinary indicating potentiometers, or with self-balancing recorders and controllers. Its response to changes of pH is rapid. The electrode may be installed directly in open, non-metallic channels or tanks of flowing solutions without fear of breakage, and it may be used in the measurement of heavy sludges, pastes, &c. Installations in paper mills have given excellent results in spite of the heavy stock encountered. Its error is not generally greater than 0·05 pH for ordinary work. The usual maintenance consists only of wiping once a day.

Unlike the other measuring electrodes, each of which follows one definite voltage-pH conversion curve, the antimony electrode follows one of several definite curves, depending on the nature and concentration of the substances in the test solution. When the proper curve is used, the pH of a solution may be determined within a limit of error of $\pm$ 0·05 pH. Conversion curves

[1] *J. Phys. Chem.*, 1930, *34*, 1295.

have been established for certain solutions. For others the relation must be determined by test. Strongly oxidizing and reducing solutions and solutions of sodium salts of high concentration cause erroneous results. The electrode should not remain continuously in acid solutions of less than 4 pH when the solution temperature exceeds 25° and even at lower temperatures should be cleaned at intervals of 6 to 8 hours in such solutions. In solutions above 11·5 pH, one hour may be required for equilibrium to be established.

The difference of potential between the antimony electrode and saturated calomel electrode varies from approximately $+ 0.10$ to $+ 0.68$ volt for a range of 2–12 pH, subject to some variation with temperature.

POTENTIOMETRIC TITRATIONS

Since the E.M.F. given by a hydrogen gas electrode depends upon the concentration of the hydrogen ions in the solution and this concentration decreases during the titration of the acid with an alkali, it is possible to follow the course of the titration by the changes in the E.M.F. of the electrode during the successive additions of measured quantities of the acid. To carry out such a titration a measured volume of the acid solution is placed in a beaker and sufficient distilled water is added to cover the stirrer (motor driven) and a hydrogen gas electrode ; the side-tube of a calomel electrode is also dipped into the solution and the E.M.F. set up by the chain is measured in the usual way. Standard alkali is then added, at the start in steps of 0·5 ml., and the E.M.F. is measured as soon as it becomes steady after each addition. When the neutral point is neared it will be found that the difference between two successive readings increases very much : as soon as this is observed the alkali must be added drop by drop, a reading being made after each addition. Again after a time it will be observed that the change in E.M.F. for successive readings decreases and additions may then once more be made by steps of 0·5 ml. When the E.M.F.s are plotted as ordinates against volume of alkali added as abscissae, a curve of the type shown in Fig. 17 (XII *) will be obtained. At the start the curve is nearly horizontal, then it bends up and becomes practically vertical and finally once more becomes nearly horizontal. The endpoint of the titration is the mid-point of the vertical part of the curve and can be determined therefrom.

From the curve it is obvious that the change in E.M.F. for a given addition of reagent becomes a maximum at the endpoint ; this maximum value of $\Delta E / \Delta X$, rate of change of E.M.F. with addition of reagent, can be calculated from the experimental figures and may be used to determine the endpoint instead of drawing the curve.

Potentiometric titrations can also be carried out for oxidation-reduction, precipitation and complex-formation reactions.

The experimental determination of a dropping electrode potential is described by Krumreich. The quinhydrone electrode (see below), is now in more general use than the former apparatus.

Quinhydrone Electrode. A very considerable simplification in the experimental technique in the titration of acids (or the determination of the pH of acid solutions) has been introduced by the use of the quinhydrone

electrode by Bijlmann to replace the more troublesome hydrogen gas electrode.

Quinhydrone is the addition product of quinone and hydroquinone in 1 : 1 mixture and can readily be prepared in a pure condition by mixing the pure alcoholic solutions and then pouring into water, in which it is not very soluble. It is now however a commercial product so that the necessity for its preparation does not arise. It is soluble in water to the extent of about 0·005 N. and with a polished gold or platinum electrode gives a sharp and definite potential which is quickly established. In acid aqueous solution quinhydrone is partially decomposed into its two components and the arrangement may be considered to act as a hydrogen electrode of very small pressure (calc. value about 10^{-24} atm.). The equilibrium may be represented by the equation
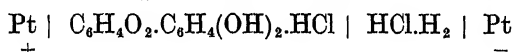
$$C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2 + H_2$$
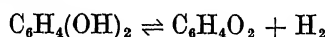
or the electromotive statement would be

$$C_6H_4(OH)_2 + 2F \rightleftharpoons 2H^+ + C_6H_4O_2$$
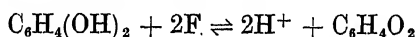
comparable with the hydrogen gas electrode reaction

$$H_2 + 2F \rightleftharpoons 2H^+$$
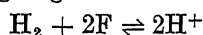
Since the equivalent hydrogen pressure of the quinhydrone electrode is so low, its E.M.F. is correspondingly high and when a chain is made up

$$Pt \mid C_6H_4O_2.C_6H_4(OH)_2.HCl \mid HCl.H_2 \mid Pt$$
$$+ \qquad\qquad\qquad\qquad\qquad\qquad\qquad -$$

the quinhydrone is the positive pole and gives an E.M.F. against the H_2 gas which is constant for all concentrations of the HCl, since this is the same for both solutions. The quinhydrone electrode can therefore be used to replace the hydrogen gas electrode. The solution under test is either shaken with solid quinhydrone or a freshly prepared aqueous or alcoholic solution is added in any desired proportion ; the faintly glowed electrode is then dropped into the solution and the reading may be taken at once. The quinhydrone electrode can be used in all acid solutions (with the reservation noted below) but fails in alkaline solutions in which pH is greater than 8. It also shows an error of some millivolts if the solution contains electrolyte in greater concentration than decimolar.

This last difficulty can be overcome if the solution is saturated with quinhydrone and in addition with either quinone or hydroquinone, by shaking with the two solid phases and arranging by means of a small well in the base of the titration cell that the electrode is covered with the solid phases during the measurements. The E.M.F.s given by the different forms of the quinhydrone electrode against the hydrogen gas electrode (at 760 mm. pressure of H_2) are as follows :

Temp.	0·005 M quinhydrone	Satd. quinhydrone and quinone	Satd. quinhydrone and hydroquinone
18°	0·7044	0·7570	0·6185
25°	0·6990	—	—

The first electrode is almost independent of the total concentration of electrolyte provided that this is not more than 0·1 molar.

The second and third electrodes are quite independent of the electrolyte concentration.

of its dissociation constant.

A saturated solution was used ; when titrated hot with sodium hydroxide and phenolphthalein, 50 ml. required 8·50 ml. of 0·1244 N.NaOH in the mean : the concentration of the acid was thus 0·02114 N. 50 ml. of the acid was used for the potentiometric titration ; about 0·2 gram of quinhydrone was added and the solution was gently shaken without bringing it in contact with the upper part of the vessel : the excess of solid was then allowed to fall into the small depression in the base of the flask and the electrode was lightly glowed and lowered into the solid. Connexion with the vessel containing the saturated calomel electrode was made with an inverted U-tube filled with agar chloride jelly made by dissolving 3 grams of agar in 50 ml. of hot water and adding saturated KCl solution to a volume of 100 ml. The whole chain was immersed in a thermostat maintained at 20° ± 0·02. The compensation method of Dubois and Raymond was used for the measurements of the E.M.F. A lead accumulator was connected to the ends of the 100 cm. wire bridge and a capillary electrometer was used. Two standard Weston normal elements were used, N_1 and N_2. N_1 was certified to have an E.M.F. of 1·0186 volts at 20°. With the aid of a commutator it was arranged that the chain was first inserted with and then against the second normal element, giving readings $N_2 + B$ and $N_2 - B$, where B is the chain reading : hence half the difference of the two readings gave the reading corresponding to the chain alone.

Then if E = E.M.F. for chain Pt — Hg

e_h = single electrode potential Pt — soln.

= E — 456·8

and $pH = \dfrac{-e_h}{58 \cdot 1}$

Thus the first reading gave

$N_1 = 485 \cdot 3$ mm., $N_2 + B = 622 \cdot 1$, $N_2 - B = 347 \cdot 8$ mm.

$B = \dfrac{622 \cdot 1 - 347 \cdot 8}{2} \quad \dfrac{274 \cdot 3}{2} = 137 \cdot 2$ mm.

$E = \dfrac{1 \cdot 0186 \times 137 \cdot 2}{485 \cdot 3} = 287 \cdot 9$ millivolts

$e_h = 287 \cdot 9 - 456 \cdot 8$

$= -168 \cdot 9$ millivolts

$pH = \dfrac{-e_h}{58 \cdot 1} = \dfrac{168 \cdot 9}{58 \cdot 1} = 2 \cdot 91$

About 1 ml. of alkali was added and the potentiometer readings were repeated. Towards the endpoint the alkali was added, of course in smaller amounts, and in this way the results shown in the table were obtained.

c.c. of alkali added	N_1	$N_2 + B$	$N_2 - B$	B	E	$- e_h$	pH	$\Delta e/\Delta x$
0·00	485·3	622·1	347·8	137·2	287·9	168·9	2·91	
								26
1·07	486·1	610·4	362·0	124·2	260·3	196·5	3·38	
								16
2·46	486·6	599·8	373·3	113·3	237·2	219·6	3·78	
								13
4·77	486·7	585·6	387·0	99·3	207·8	249·0	4·29	
								15
6·73	486·8	572·3	400·8	85·8	179·5	277·3	4·77	
								24
7·48	487·0	564·9	408·3	78·3	163·8	293·0	5·04	
								36
7·82	487·0	559·4	414·4	72·5	151·6	305·2	5·25	
								85
8·33	487·1	538·4	434·9	51·8	108·3	348·5	6·00	
								279
8·42	487·1	526·8	447·3	39·8	83·2	373·6	6·43	
								445
8·63	487·1	483·1	492·9	− 4·9	− 10·2	467·0	8·04	
								255
8·67	487·7	477·6	497·1	− 9·8	− 20·4	477·2	8·21	
								107
8·71	487·7	476·0	499·5	− 11·8	− 24·7	481·5	8·28	
								59
9·82	487·7	444·3	530·6	− 43·2	− 90·2	547·0	9·41	
								15
11·86	487·7	429·4	545·6	− 58·1	− 121·4	578·2	9·95	

In Fig. 17 (XII *) values of $- e_h$ are plotted against ml. of alkali added : the endpoint as judged by eye is marked with a cross and corresponds to 8·50 ml. of alkali in agreement with the value found by titration with phenolphthalein. In the last column of the table are given values of the differential $\Delta e/\Delta x$ calculated from columns 7 and 1. This differential gives
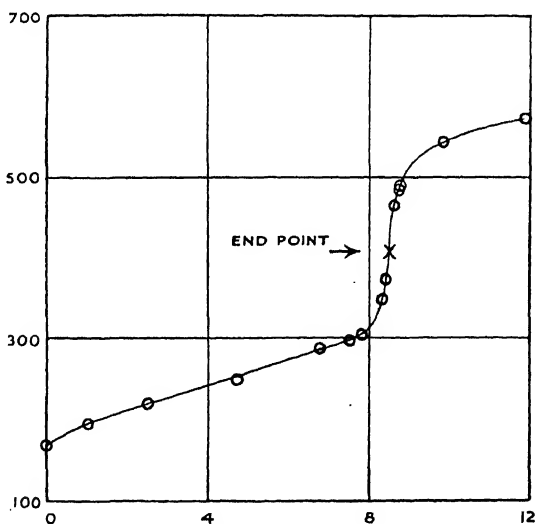

FIG. 17 (XII *)

the slope of the curve. The figures show that the curve first rises slightly, then becomes more flat and finally rises very steeply before becoming flat again. The slope is at a maximum between 8·42 and 8·63 ml. and the neighbouring figures show that it lies nearer to 8·42 than to 8·63 ml. so that it may again be put down at 8·50 ml. in agreement with the value read off from the curve.

Calculation of the Dissociation Constant. (1) An approximate value can be obtained from the half-neutralization value of pH : 8·50 ml. of alkali are required for neutralization, so that 4·25 ml. is the amount required for half-neutralization. Between the points for 2·46 ml. and 4·77 ml. the curve is seen to be a straight line so that the value of pH corresponding to 4·25 can be interpolated to be 4·17.

The concentration of the hydrogen ions at the half-neutralization point is approximately equal to the dissociation constant.

Since
$$p\text{H} = -\log C_{\text{H}^+} = 4\cdot17$$
$$\log C_{\text{H}^+} = 5\cdot83$$
$$C_{\text{H}^+} = 6\cdot76 \times 10^{-5} = \text{K}$$

The value can be obtained more correctly by means of the equation

$$\text{K} = C_{\text{H}^+}\left(\frac{x}{x_e - x}\right)$$

where C_{H^+} is the hydrogen-ion concentration calculated from the pH corresponding to the addition of x ml. of alkali and x_e is the number of ml. of alkali required for neutralization.

Thus for the second point

$$x = 1\cdot07,\ x_e - x = 8\cdot50 - 1\cdot07 = 7\cdot43,\ p\text{H} = 3\cdot38 = -\log C_{\text{H}^+},$$

whence $C_{\text{H}^+} = 4\cdot16 \times 10^{-4}$

$$\text{K} = 4\cdot16 \times 10^{-4} \times \frac{1\cdot07}{7\cdot43}$$
$$= 6 \times 10^{-5}$$

Other results are given below.

x	pH	$\text{K} \times 10^5$	x	pH	$\text{K} \times 10^5$
1·07	3·38	6·00	6·73	4·77	6·46
2·46	3·78	6·76	7·48	5·04	6·69
4·77	4·29	6·56	7·82	5·25	6·49

Mean value of $\text{K} = 6\cdot49 \times 10^{-5}$.

Ostwald found $\text{K} = 6\cdot6 \times 10^{-5}$ from the conductivity at 25°.

SECTION 2: pH COLORIMETRIC METHOD

Introduction. Since pure water is slightly dissociated into hydrogen and hydroxyl ions we have the relation

$$\frac{[H^*] \times [OH']}{[H_2O]} = k$$

but since the concentration of the undissociated water is large compared with that of the ions, it may be regarded as being constant, and we can write

$$[H^*] \times [OH'] = K_w$$

The value of K_w varies with temperature, but is approximately 1×10^{-14} at 22°, so that in pure water, where the concentration of the hydrogen and hydroxyl ions must be equal, $C_{H^*} = 10^{-7}$ and $C_{OH'} = 10^{-7}$.

In an acid solution the concentration of hydrogen ions will be greater than that in the neutral water, but since the relation $[H^*] \times [OH'] = K_w$ must still hold, the concentration of the hydroxyl ions must be correspondingly lower; for example, if C_{H^*} is equal to 10^{-4} at 22°, $C_{OH'}$ must be 10^{-10}. In a similar way with an alkaline solution $C_{OH'}$ will be greater than 10^{-7} and C_{H^*} will therefore be less. It follows that the acidity or alkalinity of any solution can be expressed by the concentration of the hydrogen ions alone. If this concentration is greater than 10^{-7} the solution is acid; if less it is alkaline. Since the possible variations in C_{H^*} are so large and therefore difficult to plot on squared paper, it is found convenient to replace C_{H^*} by another term pH which is related to the former by the equation

$$p\text{H} = \log . \left(\frac{1}{C_{H^*}} \right)$$

Thus with pure water at 22° where $C_{H^*} = 10^{-7}$

$$p\text{H} = \log \frac{1}{10^{-7}} = \log . 10^7 = 7$$

Since the value of C_{H^*} varies with temperature, the value of pH will also vary, and this variation is shown in the following table:

Temperature	pH of neutral point	Temperature	pH of neutral point
16°	7·10	26°	6·93
18	7·07	28	6·90
20	7·03	30	6·86
22	7·00	32	6·83
24	6·96	35	6·78
25	6·95	—	—

pH values are now universally used instead of C_{H^*} values.

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Determination of pH. Within the last few years the measurement of hydrogen-ion concentration has become a matter of considerable importance. It is now extensively used in the tanning and photographic industries, in dairy chemistry, in medical research, in the regulation of colour, in the manufacture of certain aniline dyes, in work on the consistency of soil and·on the conditions most favourable for plant growth.

There are several methods of measuring hydrogen-ion concentration, the chief being colorimetric, hydrogen electrode, quinhydrone electrode and glass electrode, of which the latter has many advantages over the other three. Colorimetric methods are difficult to work in opaque or coloured solutions, the hydrogen electrode is troublesome for routine control, is easily poisoned and is not applicable to oxidizers or reducers, whilst the quinhydrone electrode has a limited range of pH over which it can be operated. The glass electrode method would seem to be the pH apparatus of the future. It may be employed for determining pH of small quantities of liquids, whether coloured, easily reducible or turbid and indeed even of semi-solids such as tissues. It has an operating range of about pH 1 to pH 11. It will be considered in the next chapter.

Buffer Solutions. The standard pH solutions are the so-called buffer solutions. If 1 ml. of N/100 HCl were added to 1 litre of water the pH value would be reduced from 7 to 5, but if the same amount of acid were added to a litre of standard beef infusion of pH originally 7·0, the pH value would be changed but little. This power of certain solutions to resist a change in pH is denoted by the term buffer action. This action is found to depend on the nature and concentration of the constituents of the solution, upon the pH region in which the action is investigated and upon the nature of the acid and alkali used. The buffer solutions generally used consist of a mixture of an acid and its alkaline salt.

Reagents for Standard Buffer Solutions. Clark and Lubs' set of standard buffer solutions comprises the following :

Potassium chloride and hydrochloric acid.
Acid potassium phthalate and hydrochloric acid.
Acid potassium phthalate and caustic soda.
Acid potassium phosphate and caustic soda.
Boric acid, potassium chloride and caustic soda.

These are made up as follows :

M/5 KCl	M/5 KH_2PO_4	M/5 $KHC_8H_4O_4$
M/5 H_3BO_3 + M/5 KCl	M/5 NaOH	M/5 HCl

The solutions are made up with redistilled water and in the following way :

M/5 KCl. The salt is recrystallized three or four times and dried at 120° for 2 days.

M/5 acid potassium phthalate. 60 grams of pure caustic potash are dissolved in 400 ml. of water, and to this 50 grams of resublimed orthophthalic acid anhydride are added. The cold solution is tested for neutrality with phenolphthalein and the reaction brought to a slight pink colour by the addition of caustic potash solution or phthalic anhydride as may be neces-

sary. An amount of phthalic anhydride is then added equal to that already used and is brought into solution by heating. After filtering through a hot funnel the solution is slowly crystallized. The crystals are drained by suction and recrystallized twice from distilled water, and finally dried at 110° to constant weight.

M/5 acid potassium phosphate solution is made by recrystallizing the salt three times from water and drying to constant weight at 110°. The solution should be distinctly red to methyl red and blue to bromphenol blue.

M/5 boric acid + M/5 potassium chloride. The boric acid should be recrystallized four times from distilled water and be air-dried in thin layers between filter paper.

M/5 sodium hydroxide solution. 100 grams of pure caustic soda is dissolved in 100 ml. of distilled water in a Jena or Pyrex conical flask. The mouth of the flask is covered with tinfoil and the flask allowed to stand overnight for carbonates to settle out. A hardened filter paper is selected to fit a Buchner funnel and is treated with 1/1 caustic soda. After ten minutes the paper is washed first with absolute alcohol, then with dilute alcohol, and finally with a large quantity of distilled water. The paper is fitted to the funnel and suction is applied until most of the water has been removed. The caustic soda solution is poured on to the middle of the paper, distributing it by means of a glass rod. As soon as the liquid is filtered it is diluted to nearly 2½ litres, thus making it approximately normal, and 10 ml. of this dilute solution titrated with standard acid and then the main bulk diluted to N/5 strength, and finally titrated against quantities of 1·6 grams of purified acid potassium phthalate with phenolphthalein as indicator until a faint but permanent pink colour is obtained. A current of air freed from carbon dioxide should be passed through the solution during the titration. During the whole period of preparation of this solution contamination with carbon dioxide should be avoided as far as possible. The solution is preserved in a paraffined bottle prepared by warming the bottle, adding melted wax and rolling the bottle to get an even deposit. When the wax approaches the solidifying-point the bottle is placed upright so that the wax drains down and forms a thick layer on the bottom.

M/5 hydrochloric acid. Dilute pure hydrochloric acid to about 22 per cent. and distil. Dilute the middle portion of the distillate until it is approximately M/5 and standardize with the M/5 sodium hydroxide solution.

Standard Buffer Solutions. The reagents prepared as above are then made up into the following solutions, giving *p*H values at 22° at intervals of 0·2 *p*H as shown in Table A.

Sorensen gives a series of standard solutions comprising N/10 HCl, N/10 NaOH, N/10 glycocol and NaCl, M/15 KH_2PO_4, M/15 $Na_2HPO_4.2H_2O$, M/10 secondary sodium citrate and an alkaline borate solution.

TABLE A

1·2	50 ml. M/5 KCl and 64·5 ml. M/5 HCl diluted to 200 ml.
1·4	50 ,, ,, ,, ,, 41·5 ,, ,, ,, ,, ,,
1·6	50 ,, ,, ,, ,, 26·3 ,, ,, ,, ,, ,,
1·8	50 ,, ,, ,, ,, 16·6 ,, ,, ,, ,, ,,
2·0	50 ,, ,, ,, ,, 10·6 ,, ,, ,, ,, ,,
2·2	50 ,, ,, ,, ,, 6·7 ,, ,, ,, ,, ,,
2·2	50 ,, M/5 KH phthalate and 46·70 ml. M/5 HCl diluted to 200 ml.
2·4	50 ,, ,, ,, ,, 39·60 ,, ,, ,, ,, ,,
2·6	50 ,, ,, ,, ,, 32·95 ,, ,, ,, ,, ,,
2·8	50 ,, ,, ,, ,, 26·42 ,, ,, ,, ,, ,,
3·0	50 ,, ,, ,, ,, 20·32 ,, ,, ,, ,, ,,
3·2	50 ,, ,, ,, ,, 14·70 ,, ,, ,, ,, ,,
3·4	50 ,, ,, ,, ,, 9·90 ,, ,, ,, ,, ,,
3·6	50 ,, ,, ,, ,, 5·97 ,, ,, ,, ,, ,,
3·8	50 ,, ,, ,, ,, 2·63 ,, ,, ,, ,, ,,
4·0	50 ,, ,, ,, ,, 0·40 ml. M/5 NaOH diluted to 200 ml.
4·2	50 ,, ,, ,, ,, 3·70 ,, ,, ,, ,, ,,
4·4	50 ,, ,, ,, ,, 7·50 ,, ,, ,, ,, ,,
4·6	50 ,, ,, ,, ,, 12·15 ,, ,, ,, ,, ,,
4·8	50 ,, ,, ,, ,, 17·70 ,, ,, ,, ,, ,,
5·0	50 ,, ,, ,, ,, 23·85 ,, ,, ,, ,, ,,
5·2	50 ,, ,, ,, ,, 29·95 ,, ,, ,, ,, ,,
5·4	50 ,, ,, ,, ,, 35·45 ,, ,, ,, ,, ,,
5·6	50 ,, ,, ,, ,, 39·85 ,, ,, ,, ,, ,,
5·8	50 ,, ,, ,, ,, 43·00 ,, ,, ,, ,, ,,
6·0	50 ,, ,, ,, ,, 45·45 ,, ,, ,, ,, ,,
6·2	50 ,, ,, ,, ,, 47·00 ,, ,, ,, ,, ,,
5·8	50 ,, M/5 KH₂PO₄ and 3·72 ml. M/5 NaOH diluted to 200 ml.
6·0	50 ,, ,, ,, ,, 5·70 ,, ,, ,, ,, ,,
6·2	50 ,, ,, ,, ,, 8·60 ,, ,, ,, ,, ,,
6·4	50 ,, ,, ,, ,, 12·60 ,, ,, ,, ,, ,,
6·6	50 ,, ,, ,, ,, 17·80 ,, ,, ,, ,, ,,
6·8	50 ,, ,, ,, ,, 23·65 ,, ,, ,, ,, ,,
7·0	50 ,, ,, ,, ,, 29·63 ,, ,, ,, ,, ,,
7·2	50 ,, ,, ,, ,, 35·00 ,, ,, ,, ,, ,,
7·4	50 ,, ,, ,, ,, 39·50 ,, ,, ,, ,, ,,
7·6	50 ,, ,, ,, ,, 42·80 ,, ,, ,, ,, ,,
7·8	50 ,, ,, ,, ,, 45·20 ,, ,, ,, ,, ,,
8·0	50 ,, ,, ,, ,, 46·80 ,, ,, ,, ,, ,,
7·8	50 ,, M/5 H₃BO₃ + KCl and 2·61 ml. NaOH diluted to 200 ml.
8·0	50 ,, ,, ,, ,, 3·97 ,, ,, ,, ,,
8·2	50 ,, ,, ,, ,, 5·90 ,, ,, ,, ,,
8·4	50 ,, ,, ,, ,, 8·50 ,, ,, ,, ,,
8·6	50 ,, ,, ,, ,, 12·00 ,, ,, ,, ,,
8·8	50 ,, ,, ,, ,, 16·30 ,, ,, ,, ,,
9·0	50 ,, ,, ,, ,, 21·30 ,, ,, ,, ,,
9·2	50 ,, ,, ,, ,, 26·70 ,, ,, ,, ,,
9·4	50 ,, ,, ,, ,, 32·00 ,, ,, ,, ,,
9·6	50 ,, ,, ,, ,, 36·85 ,, ,, ,, ,,
9·8	50 ,, ,, ,, ,, 40·80 ,, ,, ,, ,,
10·0	50 ,, ,, ,, ,, 43·90 ,, ,, ,, ,,

Indicators. The indicators recommended by Clark and Lubs are as follows :

	Common name	Per cent. Conc.	Colour change	Range of *p*H
Thymol sulphonphthalein (acid range)	Thymol blue	0·04	Red-yellow	1·2–2·8
Tetrabromophenol sulphonphthalein	Bromphenol blue	0·04	Yellow-blue	3·0–4·6
Orthocarboxybenzene azodimethyl aniline	Methyl red	0·02	Red-yellow	4·4–6·0
Dibromo-orthocresol sulphonphthalein	Bromcresol purple	0·04	Yellow-purple	5·2–6·8
Dibromothymol sulphonphthalein	Bromthymol blue	0·04	Yellow-blue	6·0–7·6
Phenol sulphonphthalein . . .	Phenol red	0·02	Yellow-red	6·8–8·4
Orthocresol sulphonphthalein . .	Cresol red	0·02	Yellow-red	7·2–8·8
Thymol sulphonphthalein . . .	Thymol blue	0·04	Yellow-blue	8·0–9·6
Orthocresol phthalein ·. . . .	Cresol phthalein	0·02	Colourless-red	8·2–9·8

Stock solutions of these indicators are made by grinding 0·1 gram of the powder in an agate mortar with the quantities of N/20 NaOH indicated below, and when solution is complete diluting to 25 ml., thus giving 0·4 per cent solutions.

Indicator	Per cent Conc.	N/20 NaOH per decigram
		ml.
Phenol red	0·02	5·7
Bromphenol blue	0·04	3·0
Cresol red	0·02	5·3
Bromcresol purple	0·04	3·7
Thymol blue	0·04	4·3
Bromthymol blue	0·04	3·2
Methyl red	0·02	7·4

For use the stock solutions are diluted again to 0·02 or 0·04 per cent. Orthocresol phthalein is used in 0·02 per cent solution in 95 per cent alcohol.

Apparatus. The apparatus necessary for ordinary determinations is sufficiently simple and consists of a rack to hold the comparison solutions which are contained in the so-called 'cordite' tubes. The tubes are held by clips in an inclined position and behind the rack is a strip of white paper to form a background. With indicators which exhibit dichromatism, such as bromphenol blue and bromcresol purple, a much better match is possible when we use as light source one from which one of the colours of the solution has been eliminated. In the present instance a light from which either the red or blue is screened off is suitable.

For this purpose Clark uses a wooden box in which three or four electric lights are mounted ; the box may be lined with asbestos board. At the back a piece of tinplate is fixed as reflector and on the front is a sheet of glass over which is a sheet of translucent tracing paper, which is painted with a solution of 5 ml. of 0·6 per cent phenol red to which 5 ml. of stock K_2HPO_4 has been added. This paper is tacked in position while still wet, and effectively cuts out the blue light.

Coloured Solutions. When the pH of a coloured solution has to be found we can make use of the Walpole comparator, described under Colorimetry, or a simple substitute can be made from a block of wood by boring three pairs of vertical holes large enough to take test tubes and then boring horizontal holes through the wood so that each hole passes through one pair of the previously made holes. The tube containing the standard solution is placed in the back hole of a pair as is also the coloured solution to be tested, to which the ten drops of indicator have been added. In the hole in front of the standard solution is placed a tube containing the solution to be tested, but without indicator, while in front of the solution under test to which indicator has been added is placed a test-tube of water. On looking through the holes the light traverses in one case standard solution and then coloured solution, and in the other case coloured solution plus indicator and then water ; the effect of the natural colour of the test solution is thus balanced out. With turbid solutions a similar device is employed, using a cloud of barium sulphate to balance the turbidity.

Gillespie's Method. For approximate determinations a very simple method has been described by Gillespie.[1] In this method buffer solutions are not used ; instead, a colour standard is employed consisting of a pair of test-tubes containing together 10 drops of indicator solution, the drop ratio being varied from 1 : 9 to 9 : 1. One tube of the pair contains dilute acid and the other dilute alkali. By the term drop ratio is meant the ratio of the number of drops of indicator in the alkali tube to the number in the acid tube. The pH values are obtained from the table on facing page, taken from Gillespie's paper.

As an example, if 6 drops of methyl red are put in one test-tube with a drop of alkali (dilute) and water added up to 5·5 ml., and 4 drops of methyl red and a drop of dilute acid are put in a second tube and made up with water to the same volume 5·5 ml., the colour viewed through the side so that the light passes through both tubes is the same as that of a solution of pH 5·2 containing 10 drops of indicator in 5·5 ml. This is seen from the table, where the drop ratio 6 : 4 for methyl red is found to correspond to a pH value 5·2. The tubes are conveniently viewed through the block of wood bored in the manner described above ; while if the solution to be tested is coloured a similar block, with the lateral holes so placed that they pass through three vertical holes, is used. In one series of three holes we then have alkaline indicator, acid indicator, coloured solution under test, and in the other series solution under test with indicator added and two test-tubes of water.

Application. Buffer solutions have many applications in physical

[1] *J. Amer. Chem. Soc.*, 1920, 42, 742.

chemistry technique. In the study of the influence of storage on propellant explosives buffers are sometimes added to resist changes in *p*H which would otherwise occur with the formation of acids. In the study of reduction and oxidation potentials of chemical systems buffers are often added to the solution in which the measurements are made. In reactions in which acid or alkali is formed the *p*H can often be kept within a definite range by the use of large amounts of buffer mixture as solvent.

	Hydrogen-ion exponent for each pair of tubes						
	Brom-phenol blue	Methyl red	Brom-cresol purple	Brom-thymol blue	Phenol red	Cresol red	Thymol blue
Drop Ratio.							
1 : 9	3·1	4·05	5·3	6·15	6·75	7·15	7·85
1·5 : 8·5	3·3	4·25	5·5	6·35	6·95	7·35	8·05
2 : 8	3·5	4·4	5·7	6·5	7·1	7·5	8·2
3 : 7	3·7	4·6	5·9	6·7	7·3	7·7	8·4
4 : 6	3·9	4·8	6·1	6·9	7·5	7·9	8·6
5 : 5	4·1	5·0	6·3	7·1	7·7	8·1	8·8
6 : 4	4·3	5·2	6·5	7·3	7·9	8·3	9·0
7 : 3	4·5	5·4	6·7	7·5	8·1	8·5	9·2
8 : 2	4·7	5·6	6·9	7·7	8·3	8·7	9·4
8·5 : 1·5	4·8	5·75	7·0	7·85	8·45	8·85	9·55
9 : 1	5·0	5·95	7·2	8·05	8·65	9·05	9·75
% in indicator solution	0·008	0·008	0·012	0·008	0·004	0·008	0·008
ml. 0·1 N. NaOH per 0·1 g. portion . .	1·64	—	2·78	1·77	3·10	2·88	2·38
Produce acid colour with	0·05 N HCl	0·05 N HCl	0·05 N HCl	0·05 N HCl	0·05 N HCl	2% H_2KPO_4	2% H_2KPO_4
Quantity acid used to produce acid colour	1 ml.	1 drop	1 drop	1 drop	1 drop	1 drop	1 drop

Limitations of the Colorimetric Method.

Temperature Effect. In general this may be ignored since the error involved is not greater than that of the method : in some cases it may be large, e.g. with phenolphthalein it is 0·15 unit per degree.

Solvent Effect. When organic solvents such as alcohol are used the *p*H values determined by the colorimetric method may be much higher or much lower than those obtained with aqueous solutions.

Oxidation-Reduction. The indicators, being dyes, may have their colours altered by oxidizing or reducing agents.

Slightly Buffered Solutions. Many of the solutions encountered in industrial or scientific work may be only slightly buffered, and since indicators are either weak organic acids or bases, when these are added they may alter the *p*H value considerably : for example three drops of 0·04 per cent methyl red may alter the *p*H value of 10 ml. of pure water from 7 to 5.

Salt Effect. Errors of 0·1 to 0·2 *p*H may arise from a difference in the 'ionic strength' of the tested solution and the reference solution.

Protein Effect. This may be so large as to make colorimetric results quite unreliable unless controlled by the electrical method. This point is very important to remember in connexion with measurements on food and biological products.

Colloid Effect. This may also cause errors of several units owing to adsorption by the colloid : this effect may be expected with soil suspensions.

SECTION 3 : pH GLASS ELECTRODE METHOD

If a thin glass membrane separates two solutions of different hydrogen-ion concentration a difference of potential exists between the two sides of the glass. The difference is proportional to the ratio of the logs of the hydrogen-ion concentrations on the two sides, according to the Nernst formula. At present it is not desirable to use the glass electrode with strongly acid or alkaline solutions or with non-aqueous solutions. The difference of potential may be measured by a null point method so that the hydrogen-ion concentration of the solution on one side may be determined, if that on the other side is known.

The potential appears to depend partly upon the hydrogen-ion concentration and partly upon the concentration of the ions which the glass contains, such as sodium, calcium, &c. If the concentration of the ions of the latter were constant the cell could be used for the measurement of hydrogen-ion concentration : while if the former were constant it might have applications when a metal electrode cannot be used, as with calcium, barium, &c.

The Electrodes. Glasses, except those rich in boro-silicate, are suitable, a cheap German soft soda glass considered inferior from the glass-blower's point of view being frequently employed. MacInnes and Dole [1] devised a glass electrode having a comparatively low resistance using Corning No. 015 glass [2] containing SiO_2, 72 per cent; Na_2O, 22 per cent; CaO, 6 per cent. Morton uses a high conductivity glass made by fusing pure silica 60, anhydrous sodium carbonate 30, and calcium carbonate 10.[3] The separating membrane should be as thin as possible (0·025–0·03 mm. thick in its thinnest part). One type of cell in common use is shown in Fig. 18 (XII *). Contact with the solutions in the glass electrodes is made by means of two calomel electrodes opposed to one
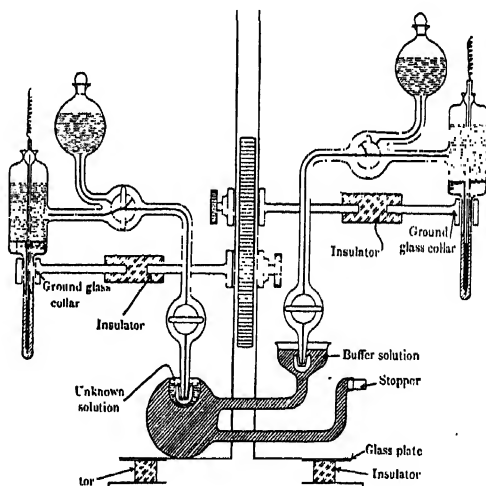
FIG. 18 (XII *)

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[1] *J. Amer. Chem. Soc.*, 1930, *52*, 29.
[2] Corning Glass Co., Corning, New York, U.S.A.
[3] This glass is obtainable from Messrs. Dixon, Devonshire Street, London.

another, as shown in figure. The level of the electrodes can be altered at will; they are supported by sleeves, ground to fit, to which are attached short lengths of glass rod fixed into insulating blocks of amberite, these being similarly fixed to the stand. Small ground caps are attached to the tips of the calomel electrode. The glass electrode is placed on a glass plate carefully insulated by amberite from the base of the stand.

Measurement of Potential. Owing to the high resistance of the glass membrane (about 10^8 ohms) a simple, potentiometric device using a sensitive galvanometer will not suffice. It is necessary to replace the galvanometer by an electrometer, an electrometer valve or a ballistic galvanometer.[1]

Electrometer Method. For this purpose a Dolazalek or Lindemann electrometer may be used, the latter being usually preferred, owing to its greater simplicity of adjustment. The arrangement of apparatus with the Lindemann electrometer is indicated in Fig. 19 (XII *). The middle point of a 60-volt battery is earthed, and the positive and negative terminals are joined to the movable contacts of a 400-ohm potentiometer, across each of which a drop of 4 volts is maintained. Leads are taken from one end of each potentiometer to the electrometer plates. A simple two-way switch enables alternate earthing and charging of the plates. The movement of the needle is observed by means of a microscope, fitted with a micrometer eyepiece. The microscope should have a $\frac{1}{2}$-inch or $\frac{1}{3}$-inch objective, and a low and high power eyepiece. The former is used
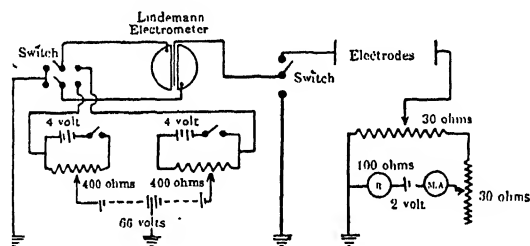
FIG. 19 (XII *)

for observing large deflections of the needle, and the latter (which has a scale) for final highly magnified observations.

To make a measurement of pH, the electrometer plates are suitably charged by adjustment of their potentials. The sensitivity of the electrometer is then tested by short-circuiting the electrode, and determining the movement of the needle for a potential of, say, 10 millivolts. The glass electrodes are then introduced, and the ends of the electrode introduced as in Fig. 18 (XII *).

The electrometer plates are then charged, the needle is earthed and its zero reading taken. It is now unearthed and the deflection reduced to zero by altering the potentiometer attached to the glass electrodes. The reading of the potentiometer gives the required E.M.F. from which the pH can be calculated.

Manipulation. Clean glass electrodes are essential. This is accomplished by cleaning with chromic acid and then soaking for 2 days in

[1] Morton, *J. Chem. Soc.*, 1931, 2977.

distilled water to remove the potential produced on the glass surface by adsorption of the strong acid. The buffer solution on one side may be a mixture of potassium phosphate of about pH 7. The unknown solution is pipetted into the inner cup, which usually has a capacity of 0·5–1 ml. The tips of the calomel electrode are flushed out with KCl before each determination, rinsed with distilled water, and then dried with filter paper. The potential E_x across the glass membrane is then determined as above. The electrode may be standardized by putting in place of the unknown solution a M/20 solution of potassium hydrogen phthalate (pH = 3·97) and measuring the potential E_s obtained. This solution has a fairly constant pH for about a month, so that it is not necessary to know accurately the pH of the potassium phosphate buffer solution which can be made up in large quantities, and stocked in ordinary glass bottles.

If E_s = Potential with phthalate in the electrode
E_x = Potential with unknown solution
E_g = Potential due to glass or calomel inaccuracy
pH$_\beta$ = Hydrogen-ion concentration of buffer solution
pH$_x$ = Hydrogen-ion concentration of unknown solution
n = Valency of hydrogen (m), F one Faraday
R, the gas constant and T the absolute temperature

$$E_s = \frac{2 \cdot 303 \mathrm{RT}}{n\mathrm{F}} \cdot (p\mathrm{H}_\beta - 3 \cdot 97) + E_g$$

$$E_x = \frac{2 \cdot 203 \mathrm{RT}}{n\mathrm{F}} (p\mathrm{H}_\beta - p\mathrm{H}_x) + E_n$$

$$E_s - E_x = \frac{2 \cdot 303 \mathrm{RT}}{n\mathrm{F}} (p\mathrm{H}_x - 3 \cdot 97)$$

Then $p\mathrm{H}_x = 3 \cdot 97 + \dfrac{E_s - E_x}{0 \cdot 0577}$ at 18°

The probable error using the Lindemann electrometer has been found to be not more than ± 0·01 pH.

Electrometer Valve Methods.[1] Many workers, notably Stadie,[2] have successfully replaced the Lindemann electrometer by the ordinary triode valve. Considerable difficulty is, however, experienced in the application of this method, owing to the fact that the grid filament resistance of the ordinary valve is of the same order (10⁸ ohms) as that of the glass electrode, so that the charge producing the E.M.F. across the glass membrane leaks away nearly as fast as it is produced, with the result that a certain time elapses before equilibrium is established. Harrison found that the time required for equilibrium was as much as 10 minutes. A new type of valve which has recently been placed on the market (Phillips Lamp Co.) eliminates the source of error—its construction being such that the grid-filament resistance is of the order 10¹⁴ ohms when a voltage of 2 volts is applied to the grid. This very high grid-filament resistance is brought about by the arrangement of the electrodes, as unlike that in the ordinary valve the filament is placed between the plate and grid. The characteristic

[1] Harrison, *J. Chem. Soc.*, 1930, 2, 1527.   [2] *J. Biol. Chem.*, 1929, *83*, 477.

curve of this valve when the grid is negative is quite straight, but has a slope of only 0·03 milliamp. per volt. For hydrogen-ion work the valve is used as indicated in Fig. 20 (XII *).
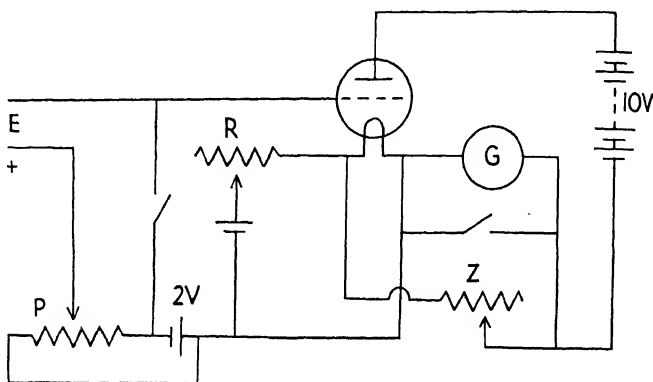
FIG. 20 (XII *)

The electrode E, and potentiometer P, are inserted in the grid circuit of the valve. A switch is placed in parallel with them. By means of the shunt circuit Z the normal anode current is reduced to zero with the switch closed, so that the galvanometer is undeflected. The working procedure in making a hydrogen-ion determination is as follows :

The electrode is inserted at E, the switch is closed and the galvanometer reduced to zero by adjusting Z. The switch is now opened, when the E.M.F. across the glass membrane, due to the pH difference, causes a change in the anode current, with consequent deflection of the galvanometer. The galvanometer needle is now brought back to its initial position by variation of the potentiometer P, the reading of the potentiometer giving the E.M.F. across the glass membrane. The galvanometer is a matter of choice, but an instrument with a sensitivity of about 1 division per microampere is just about sufficient for an accuracy of 0·02 unit over a pH range 1–12.

The Glass Electrode system of Morton (obtainable from the Cambridge Instrument Company) has considerable advantages and will be described here. High conductivity glass is used in the construction of the elec-
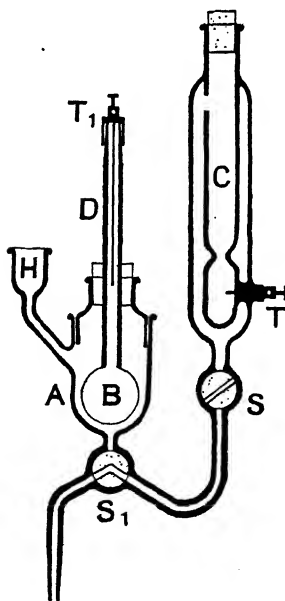
FIG. 21 (XII *)

trode whereby the resistance is reduced to the order of 2 to 10 megohms.

The E.M.F. is measured by a modification of the ballistic method of comparing E.M.F.s. In this method electrostatic shielding and exceptional

care in insulation are unnecessary. The time required for a determination is short and an accuracy of $\pm 0 \cdot 01$ pH can be obtained.

The glass electrode consists of a bulb B (Fig. 21 (XII *)) of high conductivity glass blown at the lower end of a tube D of ordinary soda glass, and filled with N.HCl saturated with quinhydrone. The upper end of the tube D is tapered and ground, and a gold-plated terminal T_1, carrying a platinum wire which dips into the solution, is fitted over the ground portion. The liquid whose pH is to be determined is introduced by means of the cup H into the vessel A. C is a saturated calomel electrode and liquid connexion with the solution in A is obtained by means of the taps S and S'. The latter is used also in draining the vessel; it is kept closed during a measurement.

The system forms a cell of the type

Pt	N.HCl quinhydrone	Glass electrode	Unknown soln. (pH$_u$)	KCl (sat.) HgCl	Hg
		B		D	M

The potential difference E between the terminals T_1 and T is the algebraic sum of the potentials at the interfaces A, B, C, D and M. The potentials at A and M are constant, that at D is assumed to be negligible and the potentials at B and C are functions of the hydrogen-ion concentrations of the solutions in contact with the two sides of the glass membrane. The observed E.M.F. is given by the equation

$$E = \frac{RT}{F}(p\text{H}_u \cdot p\text{H}_{\text{N.HCl}}) + e$$

where e is a constant which includes the potentials at A and M, together with the 'asymmetry potential', if any, of the glass membrane.

Measurement of the E.M.F.[1] A mica condenser, preferably variable in steps of $0 \cdot 1$, $0 \cdot 3$ and $0 \cdot 5$ microfarad, a discharging key and a high sensitivity ballistic galvanometer are necessary. Morton used a Cambridge Instrument Co. galvanometer having coil resistance 2,800 ohms, ballistic period (undamped) 22 sec., external critical damping resistance 70,000 ohms, factor of merit 100, ballistic sensitivity 3,430 mm. per microcoulomb at 1 metre. For standardization the vessel A is filled in succession with two known solutions pH$_k$ and pH$_k'$; the unknown solution is pH$_u$. In each case the cell is allowed to charge the condenser for a uniform period and the deflection on discharge is noted. Let the corresponding E.M.F.s and the deflections be E_k, E_k' and E_u and the deflections be D_k, D_k' and D_u respectively; then

$$k.D_k = E_k = \frac{RT}{F}(p\text{H}_k - p\text{H}_{\text{N.HCl}}) + e$$

$$k.D_k' = E_k' = \frac{RT}{F}(p\text{H}_k' - p\text{H}_{\text{N.HCl}}) + e$$

$$k.D_u = E_u = \frac{RT}{F}(p\text{H}_u - p\text{H}_{\text{N.HCl}}) + e$$

[1] Cf. *Ind. Eng. Chem. Anal.*, 1933, Edit. **5**, 278.

k is a constant and R, T and F have their usual significance. From the first two of these equations

$$\frac{p\mathrm{H}_k - p\mathrm{H}_k{}'}{\mathrm{D}_k - \mathrm{D}_k} = \frac{k\mathrm{F}}{\mathrm{RT}} = \mathrm{K}$$

here K gives the pH changes for unit deflection and

$$p\mathrm{H}_u = p\mathrm{H}_k - \mathrm{K}(\mathrm{D}_k - \mathrm{D}_u)$$

Determination of the pH Values of a Series of Buffer Solutions at 22° using the Glass Electrode. The buffer solutions to be used are those of Clarke and Lubs over the range of pH 3 to 5·2. Standard solutions of acid potassium phthalate, hydrochloric acid and sodium hydroxide are first prepared. From these standard solutions prepare the following buffer solutions, in each case using 50 ml. of the acid potassium phthalate solution and making the total volume up to 200 ml.

pH	ml. of M/5 HCl	pH	ml. of M/5 NaOH
3·0	20·32	4·0	0·40
3·2	14·70	4·2	3·70
3·4	9·90	4·4	7·50
3·6	5·97	4·6	12·15
3·8	2·63	4·8	17·70
—	—	5·0	23·85
—	—	5·2	29·95

The first and last of these are to be used as the standards of pH and the values for the other solutions are to be determined and compared with those given above.

Clean glass electrodes are essential : they should be cleaned with chromic acid and then soaked for two days in distilled water to remove the strong acid adsorbed on the surface. Inside the cell place a N.HCl solution saturated with quinhydrone after first washing out with this solution. Insert the platinum electrode. Wash out A with the first buffer solution by manipulation of the tap S′ and then fill A with the solution. The calomel electrode C is fitted up as a saturated calomel electrode as previously described, the connecting tube between S and S′ is filled with the KCl solution, contact is made between the liquid in this tube and that in A and then the tap S′ is closed (care must be taken that it does not become dry before the completion of the measurement). Place the whole cell in an air thermostat at 22°. Connect the terminals T and T_1 to the charging and discharging key, and connect the last to the 0·5 microfarad condenser and the ballistic galvanometer. Use a constant time of 1 minute (timed with a stop-watch) for each charging period and then discharge through the galvanometer and read the throw on the scale. For the present purpose the zero for the spot of light may be at the end of the scale but since the E.M.F. of the combination changes sign near pH = 7, a scale with centre zero is used when measurements are to be made over a wider range. The largest deflection in the series will be that obtained with the first solution : if the sensitivity is found not to be large enough a larger condenser is used,

still with the same charging time. When a satisfactory sensitivity has been obtained take the mean of three readings. Wash out the cell and repeat the experiment with each of the solutions in turn, making no further alterations in the capacity or the time of charging.

As an example of the calculation the following results were obtained in an experiment :

pH	3·0	unknown	5·2
Deflection in mm. .	394	289	200·5

here $p\mathrm{H}_k = 3\cdot0$, $p\mathrm{H}_k{}' = 5\cdot2$, $\mathrm{D}_k = 394$, $\mathrm{D}_k{}' = 200\cdot5$ and $\mathrm{D}_u = 289$.

$$\mathrm{K} = \frac{p\mathrm{H}_k - p\mathrm{H}_k{}'}{\mathrm{D}_k - \mathrm{D}_k{}'} = \frac{3\cdot0 - 5\cdot2}{394 - 200\cdot5} = -\frac{2\cdot2}{193\cdot5} = -0\cdot01137$$

$$\begin{aligned}p\mathrm{H}_u &= p\mathrm{H}_k - \mathrm{K}(\mathrm{D}_k - \mathrm{D}_u) \\ &= 3\cdot0 + 0\cdot01137 \times 394 - 0\cdot01137\mathrm{D}_u \\ &= 7\cdot48 - 0\cdot01137\mathrm{D}_u\end{aligned}$$

and in the case of $\mathrm{D}_u = 289$

$$\begin{aligned}p\mathrm{H} &= 7\cdot48 - 0\cdot01137 \times 289 \\ &= 7\cdot48 - 3\cdot286 \\ &= 4\cdot19\end{aligned}$$

The Beckman pH meter (National Technical Laboratories, Pasadena) uses the principle of the potentiometer system in which the voltage of the electrode system is balanced against that of a standard cell. To indicate balance a vacuum-tube amplifier, acting as a null instrument, is used, thus permitting a high sensitivity without drawing appreciable current from the electrodes. The electrode system consists of a glass electrode and a saturated calomel electrode : the glass electrode is small and strong, so that it can be wiped off after using. The calomel electrode makes contact through a carefully ground-glass joint and the electrodes are so small that only 2–3 ml. of solution are required. A micro-glass electrode is also available so small that determinations can be carried out on samples as small as 0·005 ml.

A temperature compensator is provided and a zero adjuster for the asymmetry potential of the glass. The dial is calibrated over the range from 0–12·5 in steps of 0·1 and the meter is said to be accurate to 0·01 unit.

An adaption can be used for free flowing aqueous solutions with the range 0–9·5 pH and at temperatures between 10–40° ; this is especially useful with slightly buffered solutions which must not be exposed to the air.

SECTION 4: pH CONTROL

This method of control is now being increasingly used since in many processes the maintenance of a correct pH value is of great importance. In the nickel-plating industry, for example, it is essential that the pH of the bath should be between the limits of 5·2–5·8 pH. If the pH falls the current efficiency is lowered by the evolution of hydrogen; if the pH rises above 6, the coating of nickel becomes poor and is liable to flake. If an electrode system is permanently fixed in the bath and connected to a potentiometer situated in the laboratory, any additions of sulphuric acid or nickel carbonate required can be determined by the chemist in charge.

The first point is the choice of a suitable electrode: the usual electrodes are:

Electrode	pH range
Hydrogen .	the whole range
Quinhydrone	up to pH 7·5
Antimony .	2–13 pH
Glass . .	up to pH 10

The hydrogen electrode gives the highest accuracy, but is very susceptible to the presence of colloidal matter and the platinum coating has frequently to be replaced: hence it is mainly used now only for preparing standard solutions to be used in checking other electrode systems.

The quinhydrone electrode is very widely used owing to its trustworthy results and its simplicity, but it is limited in that it cannot be used in solutions having a pH greater than 7·5.

Both the above electrodes will readily give results correct to 0·02 pH, but for this degree of accuracy exact temperature control is necessary since an error of 1 per cent. is introduced by a temperature error of 3°.

For industrial use the antimony electrode is very promising owing to its wide range, 2–13 pH, and to the facts that it is not easily 'poisoned' and requires very little attention to keep it in good working condition. Its accuracy is not greater than 0·05 pH.

The glass electrode is not so simple to use, but can be used with solutions containing colloidal matter or strong oxidizing or reducing substances which interfere with the other electrodes.

The electrode system may be permanently fixed in the tank or may be connected by way of a tap so as intermittently to bleed a pipeline conveying the solution under test, or, of course, samples may be taken for examination in the laboratory.

With the exception of the glass electrode it is possible to use the other electrodes at a considerable distance, e.g., several hundred yards, from the measuring instrument provided that the connection is made by high-class electric-lighting wire, either lead-covered or placed in conduit.

Suitable potentiometers are made by the Cambridge Instrument Co., as is the apparatus for automatic control described below.

The principle is not limited to *p*H control and, for example, the method is used in the determination of chloride ion in connection with the contamination of boiler feed water with sodium chloride from the condenser water. In this case a silver-silver chloride electrode system is used.

Automatic Recording and Control. A recording controller may be situated in the control laboratory and connected to the electrode system and the control motor driving an acid valve or the like. When a glass electrode is used a special thermionic valve unit is required and this must be situated close to the electrode system; the rest of the apparatus may then be at a distance.

The recording controller is equipped with a set of contacts which determine the direction of operation of the valve motor whenever the recorder pen leaves the desired *p*H. The contacts can be moved over the range of the recorder by operating a knob outside the case; in this manner the control point may be changed while the recorder is working. In addition to these ' directional' contacts, a further pair is fitted and driven continuously by the recorder motor, and determines for how long and how often the valve motor shall run. The contacts may be given a wide range of adjustment and the valve control motor can be arranged to open the valve fully from the closed position in either 15 minutes or $4\frac{1}{2}$ hours. In this way the valve can be adjusted to very fine limits in either direction of its travel.

The type and size of valve to be used and the position of the sampling point will depend upon a number of factors which must be considered in each individual case, but in general it may be stated that efficient stirring is necessary and the sampling-point should be remote from the valve.

The Cambridge *p*H Meter. The Cambridge *p*H meter, suggested by C. Morton for use with the glass electrode without an electrometer, provides a direct-reading instrument calibrated in *p*H units which requires no technical knowledge and no calculations or reference to tables. The circuit employed has been chosen to eliminate the troubles known to exist in most instruments employing thermionic valves. Since the valve is arranged to operate as a null point detector, the calibration is independent of the valve characteristic and remains unchanged with ageing. The instrument is automatically compensated for changes in grid bias and anode voltage.

The switches, rheostats, pointer galvanometer and terminals are mounted on a metal top board, and the valve, which is of a robust type, is effectively protected by mounting it beneath this top board. The galvanometer serves to standardize the *p*H scale against a Weston normal cell contained in the instrument and to indicate when balance is obtained. A resistance is fitted by means of which any variation in the E.M.F. of the solution due to the temperature is compensated. The accuracy is independent of the resistance of the glass electrode. The whole of the current taken by the instrument, including grid and anode voltages, is supplied by a 12-volt accumulator. The instrument is calibrated for a range of 14 *p*H units, each division on the circular dial corresponding to 0·02 *p*H. A simple

range switch enables readings in millivolts to be obtained, the range being 0–1,400 millivolts ; readings are given directly to 2 millivolts, or by estimation to 1 millivolt. A 'depress to read' tapping key enables the balance position to be watched and if necessary adjusted up to the moment of reading, thus eliminating the effect of valve drift. This instrument is eminently suitable for routine industrial tests, while its accuracy and adaptibility to various forms of electrodes renders it valuable for research purposes on practically all types of solutions and substances.

. **Universal Direct-Reading Hydrogen-ion Potentiometer.**[1] This instrument may be used with any reversible type of hydrogen-ion cell and at any temperature. A single scale, by means of which readings may be obtained either in millivolts or in pH units, is provided ; the ranges are 0–1,400 millivolts and 0–14 pH units respectively, readings being obtained directly to 1 millivolt or 0·01 pH unit. An electrometer triode valve is employed, enabling readings to be obtained with the glass electrode, the use of which is rapidly extending in industry. The dial readings in all cases give directly the actual pH value of the solution in contact with the electrodes, no correction being required. All such corrections, including compensation for temperature and barometric pressure when required, correction for the asymmetry potential in the case of the glass electrode, and correction for any error in the potential of the reference electrode (due to contamination or to the use of impure electrode materials), are automatically included in the single standardizing operation. The calibration of the instrument is permanent and independent of the characteristics of the valve.

General Description. The electrical circuit is shown in Fig. 22 (XII *). It will be seen that the potentiometer and filament currents are supplied from a common source, and that the grid bias and anode voltage are provided by the voltages dropped across resistances included in the common series circuit. This main series circuit includes also a fixed resistance and a slide wire (the temperature corrector), across which the standard cell and galvanometer may be connected for purposes of standardization. The temperature corrector is calibrated in such a manner that, when the dial is set to the temperature $t°$, and the main current rheostat adjusted so that the galvanometer is undeflected, the voltage drop across each main division of the potentiometer (corresponding to 1 pH unit) is equal to 0·000198322T volt, where $T = 273 + t$. It is clear that this standardization will define also the grid bias, filament current and anode voltage.

The indicator electrode (i.e. the electrode immersed in the solution under test) is connected to the grid of the valve, and the reference electrode to the slidewire, regardless of the polarity of the hydrogen-ion cell. When the apparatus is first put into use the electrodes are standardized to compensate for any error in the potential of the reference electrode ; for this purpose the cell is filled with a buffer solution of known pH value. The potentiometer dials having been set to read this known pH value, the switch is thrown to the 'test' position, and the galvanometer pointer is brought to a convenient point on the scale by means of the anode current-balancing controls. The effect of this adjustment is to establish an arbitrary

[1] Morton and Best, *J. Soc. Chem. Ind.*, 1933, *52*, 6T.

zero to which all subsequent measurements with the same electrodes and at the same temperature are referred. Considerations of the wiring diagram will make it clear that standardization of the main potentiometer current will thereafter define also this arbitrary zero, and no adjustment of the anode current balancing controls will be required unless the operating conditions (as regards temperature and type of electrodes) are changed.

For routine determinations the procedure is extremely simple. The cell is filled with the solution under test, and the potentiometer dials are adjusted so that the galvanometer pointer is brought back to the arbitrary zero ; the dial readings then give directly the *p*H value of the solution under examination. That this must be the case is clear from the consider-
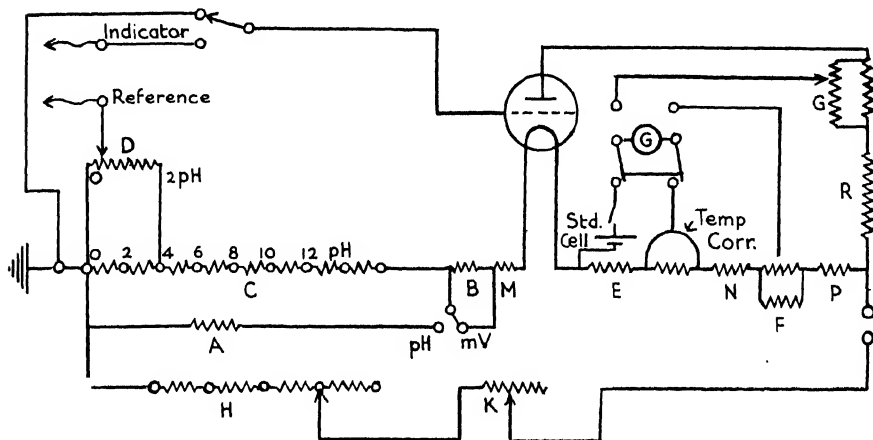
FIG. 22 (XII *)

A. Potentiometer shunt resistance, 19–43 ohms.
B. Potentiometer series resistance, 5–862 ohms.
C. Main potentiometer arm, 8 coils, 2 ohms resistance per coil.
D. Potentiometer slidewire, 4 ohms.
E. Standardising resistance, consisting of a fixed resistance of 9,833 ohms in series with a slidewire of 0–70 ohms.
F. G. Anode current-balancing resistances ; combined values, 15 ohms and 250 ohms respectively.
H. Coarse rheostat, 4 coils, each of 5 ohms resistance.
K. Fine rheostat, 6 ohms.
M. Resistance supplying additional grid bias, 8 ohms.
N. P. Resistances supplying additional anode voltage, 35 ohms and 10 ohms respectively.
R. Anode resistance, 10,000 ohms.

ation that, whatever type of reversible hydrogen-ion cell is used, the potential of the indicator electrode (and therefore that of the grid of the valve) becomes more negative by $0 \cdot 000198322T$ volt for unit increase in the *p*H value of the solution. Hence to restore the anode current to the original value, i.e. to bring the pointer back to the arbitrary zero, the positive potential imposed by the potentiometer must be increased by $0 \cdot 000198322T$ volt (one main division of the potentiometer) per unit *p*H increment.

When readings in millivolts are required a similar procedure is followed, but the ordinary rules of polarity are observed. The negative pole of the cell (which may be either the indicator or the reference electrode) is connected to the grid, and the positive pole to the potentiometer. The standardization of the main potentiometer current is carried out as described above, but with the temperature corrector permanently set to 20° and with the

potentiometer unshunted; when this adjustment is completed the fall in potential along each main potentiometer coil is 200 millivolts. In order to establish an arbitrary zero to which subsequent measurements may be referred, the grid is earthed by means of the grid circuit switch, and with the standardizing switch in the 'test' position the anode current-balancing controls are adjusted so that the pointer of the galvanometer is brought to a convenient position on the scale. When this adjustment has been made, for a given valve, the standardization of the potentiometer current will automatically define also the arbitrary zero until such time as the valve characteristics change owing to ageing; a slight readjustment will then be required.

The potentiometer current having been standardized, the grid circuit switch is thrown to its alternative position, thus applying the unknown E.M.F. (in series with the opposing potential derived from the potentiometer) to the grid of the valve. The potentiometer controls are adjusted so that the galvanometer pointer again rests over the arbitrary zero, and the dial readings are then equal and opposite to the unknown E.M.F.

Universal Electrode System. The electrode system consists of a saturated calomel electrode connected, by means of a tube filled with saturated potassium chloride solution, to an electrode vessel into which the solution under test is poured. The electrode vessel may be provided with interchangeable electrode assemblies, in order that the system may be used with the hydrogen, quinhydrone or glass electrodes. The galvanometer is a sensitive unipivot pointer instrument, and this, with the standard cell and valve, are contained within the instrument case, and no accessory is required other than a small 12-volt accumulator.

Application to Various Electrodes. The instrument may be described as universal in application in the sense that, unlike earlier direct-reading instruments, it may be used with any type of reversible indicator electrode (hydrogen, quinhydrone, glass, &c.) and with any reference electrode (calomel, silver-silver chloride, Veibel's electrode, &c.).

1. *The Hydrogen and Quinhydrone Electrodes.* In the case of these electrodes, the use of an electrostatic method of measurement (such as is employed in the instrument now described) is not essential; the method has, however, several advantages. Polarization is eliminated, and on this account equilibrium is more rapidly approached. The sensitivity of the indicating instrument is independent of the electrical resistance of the cell; this makes it possible to interpose several closed stopcocks between the indicator and reference electrodes and thus to ensure freedom from contamination during a lengthy titration. Moreover, valuable information in regard to the performance of the electrodes may be gained by observing the movements of the galvanometer pointer as equilibrium is approached. 'Poisoning' or reduction at the hydrogen electrode is indicated by erratic movements of the pointer, or by a rapid drift when the hydrogen supply is cut off; in such cases the glass electrode should be employed. As is well known, the hydrogen electrode gives erroneous results in the presence of oxidizing or reducing agents or of salts of metals more 'noble' than hydrogen. The quinhydrone electrode is also affected by powerful oxidizing or reducing agents, and is inapplicable in alkaline solutions.

2. *The Glass Electrode.* In view of the fact that the glass electrode is unaffected by colloidal materials, suspended precipitates, powerful oxidizing and reducing agents, and electrode ' poisons ' in general, it would appear to be the ideal hydrogen-ion indicator for industrial purposes. In the practical design of the instrument, care has been taken to maintain unimpaired the valuable electrical characteristics of the electrometer triode valve which is incorporated in the circuit ; in consequence, it is possible accurately to measure the E.M.F. of a glass electrode little thinner than a test-tube and having a D.C. resistance of 100,000 megohms. For ordinary purposes the range over which direct reading in pH units is permissible may be taken as pH 2–10 ; in the presence of high concentrations of sodium or other univalent metallic ions, however, the upper limit is reduced to about pH 9·5. The range may be extended in either direction by calibrating the electrode by means of buffer solutions, and plotting the dial readings against the known values of the pH of the reference solutions. The existence of the ' asymmetry potential ' does not present any difficulty since, as already explained, correction for this potential is automatically included in the standardizing adjustment.

Erroneous results are obtained with metal-metallic oxide and other irreversible electrodes, the E.M.F.–pH relationship of which is non-linear and unstable.

CHAPTER XIII *

DIELECTRICS [1]

SECTION 1 : DIELECTRIC CONSTANTS

DIELECTRIC Constants. The dielectric constant occurs in the expression for the force between two charges e and e' separated by a distance d; $f = \dfrac{ee'}{\varepsilon d^2}$, in which ε is a constant depending on the medium separating the two charges. The constant also arises in the expression for the capacity of a condenser C which is proportional to the dielectric constant of the medium between its plates, i.e. $C = \varepsilon C_0$, where C_0 is the capacity of the condenser with a vacuum between its plates. It is by means of this relation that measurements of the dielectric constant are made.

Nature of the Polarization and Dipole Moment. If we consider an isolated atom as, for example, the atom of a gas, consisting of a positive nucleus with the electrons circling round·it, it is evident that without an external field the centre of gravity of the positive electricity and the centre of gravity of the negative electricity coincide. If a field is introduced it is evident that the electrons can shift in regard to the nucleus, the centres of gravity of positive and negative electricity do not
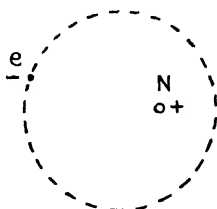
FIG. 1 (XIII *)
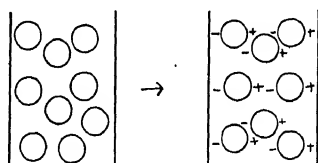
FIG. 2 (XIII *)

coincide then any longer, 'polarization' occurs; the atom obtains an 'induced dipole-moment' which disappears as soon as the field stops working Figs. 1 (XIII *) and 2 (XIII *).

It goes without saying that not in all atoms equal moments are induced by equal field intensities, i.e. the polarization depends on the nature of the atom; generally, a large atom is polarizable in a stronger degree than

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[1] The original chapter on Dielectric Constants (2nd ed.) has been revised and mostly rewritten by Dr. P. Cohen Henriquez. Messrs. P. & J. Kipp and Zonen have translated the original and prepared the drawings.

a small atom. Now, if two equal atoms combine to a molecule (e.g. Cl_2, O_2) the symmetrical relations are such that also in that case no permanent moment arises.

If, however, two unequal atoms combine (e.g. H with Cl), the centres of gravity of positive and negative electricity will then not coincide in the molecule; a 'permanent dipole' has arisen. The atoms have a different 'electronic affinity' which in the extreme case may give rise to an electron of one atom jumping to the other (in the case of the pure salts).

The distance of the centres of gravity of positive and negative electricity multiplied by the charges is the 'dipole moment' (μ) of the molecule.
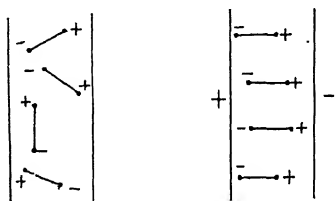
FIG. 3 (XIII *)

As will be easily understood and as is shown in Fig. 3 (XIII *), in an electric field the polar molecules tend to orientate their axes in the direction of the field.

The tendency of the polar molecules to assume this orientation is opposed, however, by their thermal agitation, and in some cases by the forces which the molecules exert upon one another (e.g. in the case of crystals). In the gaseous form the molecules are comparatively far apart and they can orientate readily; this is also the case in dilute solutions in non-polar solvents. So we see that the dipole-molecules can supply their share in the polarization by directing themselves.

From this it follows that the total polarization can be traced to a shift of the electrons in regard to the nucleus and to the orientation of the dipoles. Besides, we have to reckon with the fact that the dipole can be 'stretched' or 'compressed' by the field; this effect, too, contributes to the polarization and is called 'atomic polarization'; it is, however, frequently to be neglected.

Thus, the total molecular polarization (P) of a substance is composed of :

(1) the electronic polarization which originates in the shifting of the electrons in the atom with respect to the nucleus of the atom ($_EP$) ;

(2) the so-called 'atomic polarization' caused by the fact that the distance between two atoms can be made larger or smaller by means of an electric field; ($_AP$)

(3) the polarization through orientation of the dipoles ($_OP$).

Hence the formula :

$$P = {_E}P + {_A}P + {_O}P \qquad (1)$$

The polarization in the dielectric is defined as the electric moment per unit volume and *Clausius* and *Mosotti* obtained an expression for the polarizability of one mole of *non-polar* substance.

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = \frac{4\pi N a_0}{3} \qquad (2)$$

where P = molar (or molal) polarization [1]
   ε = dielectric constant
   M = molecular weight
   d = density
   N = Avogadro's number
and a_0 = molecular polarizability, i.e. the moment induced in one single molecule by a field of unit strength.

According to the formulae of *Maxwell* the dielectrical constant is always equal to the square of the refractive index, provided, of course, that both are measured for the same wave-length. Thus : $\varepsilon = n^2$.

From Maxwell's relation between the index of refraction and the dielectric constant, equation (2) becomes (see Vol. I, p. 124)

$$_E P = \frac{n^2 - 1}{n^2 + 2}\cdot\frac{M}{d} = \frac{4\pi N a_0}{3} . \qquad . \qquad . \qquad . \qquad (3)$$

showing that the polarization due to the induced dipoles (the electronic polarization $_E P$) is equivalent to the molecular refraction. The theory of Clausius–Mosotti was extended by *Debye*,[2, 3, 4, 5, 6] who assumed the existence of permanent dipoles in the molecules of certain substances, independent of the external field. As already said, such molecules are termed polar and denoting their permanent moments by μ Debye obtained an equation for the polarization in a medium composed of such molecules

$$P = \frac{\varepsilon - 1}{\varepsilon + 2}\cdot\frac{M}{d} = \frac{4\pi N a_0}{3} + \frac{4\pi N}{3}\cdot\frac{\mu^2}{3kT} \qquad (4)$$

where k = molecular gas constant $1\cdot372 \times 10^{-16}$
and   T = absolute temperature

The term on the right-hand side of the equation is the contribution to the polarization of the molecules owing to their permanent dipoles. Obviously if $\mu = 0$, the molecules are non-polar, and thus this equation reduces to the simple Clausius–Mosotti expression (2).

When the dielectric constant and density of a substance are measured in the gaseous condition or in extremely dilute solution in a non-polar solvent, the polarization should conform to Debye's equation, which is a function of the absolute temperature and may be written

$$P = a + \frac{o}{T} \text{ or } PT = aT + b$$

If PT is plotted against T, a straight line is obtained of slope $a = \dfrac{4\pi N}{\partial}$

and intercepting the vertical axis in $b = \dfrac{4\pi N\mu^2}{gK}$. Theoretically, it is thus

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[1] Strictly speaking, P is not the molal *polarization*, but the molal *polarizability*, but one uses always the first denomination.
[2] Debye, *Polar Molecules*, Chap. 1. New York Chemical Catalogue, 1929.
[3] Smyth, *Electric Moments*. New York, 1931.
[4] J. Errara, *Le moment électrique en chimie et en physique*. 1935.
[5] Fuchs and Wolff, *Dielektrische Polarisation*. Leipzig, 1935.
[6] Grignard, *Traité de Chimique Organique*, 1936, *11* (1), 479.

possible to determine the electric moment of a molecule by observing the dielectric constant and the density of a substance in the gaseous condition or in dilute solution and plotting the product of the polarization and the temperature against the temperature, but many practical difficulties impede the general use of this method. To the methods, practically used, we shall return below.

Dependency of the Polarization upon Frequency and Viscosity. Let us consider what happens if we apply a high-frequency alternating current field to a dipole substance.

In Fig. 4 (XIII *) the polarization is very schematically plotted against the frequency.

Normally, the ε is measured in a region quite on the left-hand side of the figure.

If we increase the frequency, we shall come into a region in which the dipoles are no longer able to follow the rapid changes of the field (for the orientation takes up a measurable time). The polarization through orientation does not occur any more and the dielectrical constant decreases. If the frequency of the field is raised still more, the atomic polarization, too, disappears and, finally, this will even be the case with the electronic
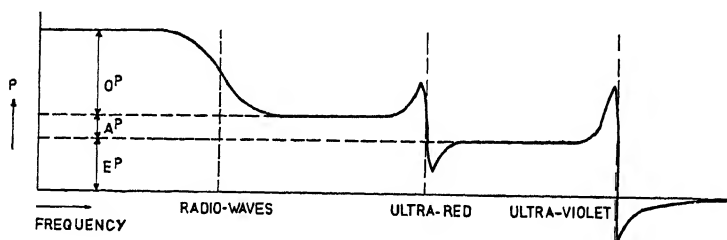
FIG. 4 (XIII *)

polarization, if the frequency of the field has become so great that even the electrons are too inert to follow the field.

The second region of anomalous dispersion lies with frequencies of the ultra-red, the third region most often with frequencies greater than those of visible light.

This is not the right place to go further into the subject of the remarkable process of the curve in the second and third region of anomalous dispersion, nor can the phenomena further be discussed here that these regions happen to coincide with absorption regions. Naturally, it is, for practical reasons, not possible to measure the dielectrical constant in these regions; the refractive index is measured instead.

With most fluids the first region of anomalous dispersion lies with wavelengths of a few meters or below. With these small wave-lengths it is difficult to perform measurements of the dielectrical constant, so that only very few substances have been investigated as yet in this region. It is, however, obvious that the region of anomalous dispersion can be removed to the side of the long wave-lengths by raising the viscosity for the inertia with which the dipoles direct themselves is the greater in proportion to the viscosity being also greater.

In solids the 'micro-viscosity' is frequently so great as to render it impossible for the dipoles to direct themselves. This, however, is not always the case and it is exactly those other cases which are extremely interesting. Below we shall return to them.

The principal methods of measuring dielectric constants involve the determination of the capacity of a condenser empty, and filled with the substance, the constant being given by the ratio,

$$\frac{\text{Capacity of condenser full of substance}}{\text{Capacity of empty condenser}}$$

Bridge Method. If four perfect (no-leak) condensers are arranged in the form of a Wheatstone bridge as in Fig. 5 (XIII *), no current passes through the telephone when $\dfrac{C_1}{C_2} = \dfrac{C_3}{C_4}$.

One of these capacities C_4 is made in the form of a cell so that its capacity can be measured first with air, and then with the substance under investigation between its plates.

Difficulty is occasioned when the substance has appreciable conductivity, and it behaves as a capacity with a resistance in parallel. In such cases adjustment of the capacities balances the bridge to give a minimum sound in the phones, but a small current passes through the phones owing to the unequal resistance in one arm of the bridge. It becomes necessary, therefore, to balance out this resistance by placing high variable resistances in parallel with C_3 and C_4 and adjusting them till the resistances of the

FIG. 5 (XIII *)

two arms are equal, the minimum current being then reduced to zero.
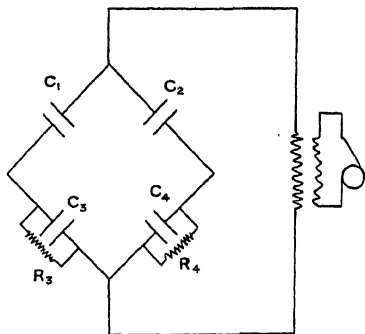
Various frequencies have been employed in such bridge determinations varying from audible frequencies, to radio-frequencies of 10^8 or more.[1, 2]

In one sense it is an advantage to employ high frequencies, as the relative amount of the current flowing in the capacities, compared to that through the resistances, increases as the frequency increases, and the effect of resistance in the measuring cell becomes of less importance. On the other hand, high frequency current in the bridge introduces complicating factors, such as external capacity and induction effects which are negligible at low frequencies.

Substitution Method. An alternative method of employing the capacity bridge consists in placing an accurate variable condenser C_4 in parallel with the cell containing the material. The bridge is first balanced by adjustment of C_4. The cell is then placed in parallel with the condenser, and C_4 is again adjusted for balance. The difference between the two readings of C_4 gives the capacity of the cell. This method is more suitable for use with high frequency current, and has been employed by Smith,

[1] Hertwig, *Ann. der Physik.*, 1913, *42*, 1049.   [2] Joacim, *Ibid.*, 1919, *60*, 570.

Morgan, and Boyce [1] for measurements at frequencies of 5×10^5, for details of which the original paper should be consulted.

Capacity Bridge. A capacity bridge working on the above principle has been designed by Smith, Morgan and Boyce, in which particular attention is paid to electromagnetic shielding. The bridge is supplied with a high-frequency current from a valve generator, and the telephone is replaced by a detector amplifier and telephone, so that ease of setting the bridge is greatly increased. The accuracy of setting the bridge is 1 micro-microfarad.

Resonance Method. The resonance method is particularly suitable for the determination of the dielectric constant of fairly conducting liquids.

In a circuit, Fig. 6 (XIII *), composed of inductance L, capacity C, and resistance R all in series, the effective current is

$$I = \frac{E}{\sqrt{R^2 + \left(2\pi fL - \dfrac{1}{2\pi fC}\right)^2}}$$

where $f =$ the frequency of the alternating source. This current obviously has a maximum value, when

$$2\pi fL = \frac{1}{2\pi fC} \text{ or } f = \frac{1}{2\pi\sqrt{LC}}$$

The frequency given by this equation is the natural frequency of the circuit and oscillations induced in a circuit produce a large relative current. When their frequency and the natural frequency of the circuit are the same, the condition is called resonance.

Walden, Ulrich, and *Werner* [2] have made use of the principle of resonance in the measurement of dielectric constants. Their apparatus is shown in Fig. 6 (XIII *). Oscillations are generated in circuit I, and induce oscillations in circuit II. The capacity C' is altered until the current reaches a maximum value corresponding, as shown by the detector circuit III coupled to circuit II. The dielectric cell is next placed in parallel with C_1, and the latter is adjusted until resonance is again attained. The difference in readings of the condenser
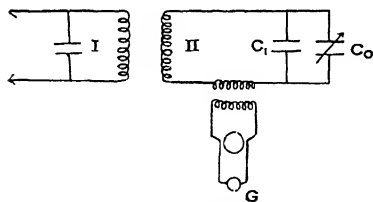
FIG. 6 (XIII *)

C_1 is equal to the capacity of the cell. The detector in circuit III consists of a thermo-vacuum element and uni-pivot—galvanometer.

Heterodyne Beat Method. [3] In this method two valve oscillators are loosely coupled, so as to produce beats of audible frequency. The arrangement of apparatus is shown in Fig. 7 (XIII *). The capacity and inductance in oscillator I are adjusted to give a frequency of 10^6 cycles, those of oscillator II producing a frequency of 1,000–2,000 cycles. The beats having a frequency of 2,000 cycles are induced in circuit III, and are amplified by the three-stage valve amplifier, producing a strong note in the telephone.

[1] Smith, Morgan and Boyce, *J. Amer. Chem. Soc.*, 1928, *50*, 1536.

[2] Walden, Ulrich and Werner, *Z. physik. Chem.*, 1925, *115*, 177.

[3] Williams, *J. Amer. Chem. Soc.*, 1900, *52*, 1831; *Phys. Review*, 1929, *24*, 400.

If the capacity of the condenser in II is lowered the frequency of the beats is lowered, until finally no note is obtained in the phone. The point of inaudibility is extremely sharp. The difference in reading of the capacity C_2 gives the capacity of the cell. Difficulty is occasioned in this method in the case of substances of appreciable conductivity as the conductance may so affect the frequency that the difference between the two condensers' readings with the cell in and out does not measure the effect of a true capacity.

Heterodyne Beat Method for Gases. The accuracy of the heterodyne beat method is greatly increased by employing a third source of oscillations, giving a note of the same frequency as that of the beats produced from oscillators I and II. When this condition is attained no note is heard in the telephone. The dielectric cell is now inserted in parallel with the variable condenser of oscillator II, and the frequency of the beats is altered. The variable condenser is then adjusted until the frequency of the beats is the same as before, i.e. until silence is again obtained in the telephone. The change in reading of the variable condenser measures the capacity of the dielectric cell. Extreme accuracy is attainable by this method corresponding to a change of one in the frequency of the oscillator. *Zahn* [1] has employed the method for his work on the dielectric constant of gases.

FIG. 7 (XIII *)

Ultra-Micrometer Method. A method of determining dielectric constants of gases based on Dowling's recording ultra-micrometer has been
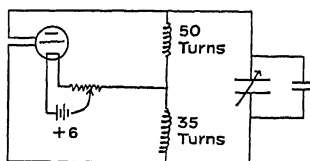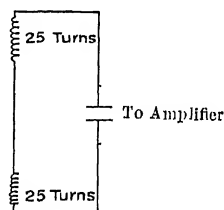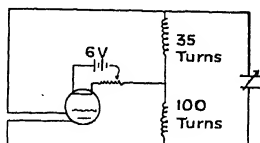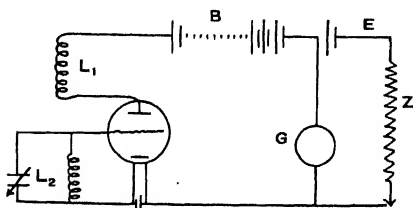
FIG. 8 (XIII *)
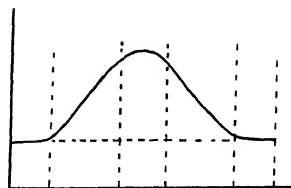
FIG. 9 (XIII *)

employed by *Carman* and *Lorance*.[2] It consists of a valve with inductance L_2 and a capacity in the grid circuit arranged so as to generate undamped oscillations of any desired frequency (Fig. 8 (XIII *)). In the plate circuit there is joined in parallel an adjustable resistance Z and galvanometer G—

[1] Zahn, *Phys. Rev.*, 1924, *24*, 400.
[2] Carman and Lorance, *Phys. Rev.*, 1922, *20*, 715.

so that the normal plate current can be balanced—thus permitting the use
of a sensitive galvanometer. A variation of the capacity gives a variation
of the steady plate current over certain ranges, M_1, M_2 (Fig. 9 (XIII *)),
within which the H.F. oscillation amplitude depends on the magnitude of
the capacity. The two portions M_1 and M_2 of the curves show that over
these ranges a linear relation exists between plate current and capacity.
In the arrangement employed by Carman and Lorance a change in capacity
of 1 cm. corresponds to a change in plate current of $2 \cdot 1 \times 10^{-7}$ amps., so
that changes in capacity of a hundredth of a centimetre can be recorded.

In measuring the dielectric constant of gases two air-condensers, one
of fixed capacity (3,580 cm.), the other of adjustable capacity, are inserted
in parallel in the grid circuit. The larger condenser is placed in a glass
cylinder which is exhausted and into which the different gases can be
introduced. The whole apparatus is enclosed in an earthed cage. The
change in capacity of the ' air ' condenser in a vacuum and with the given
gas as dielectric is measured direct, in terms of galvanometer deflections,
the small adjustable condenser being used for calibration.
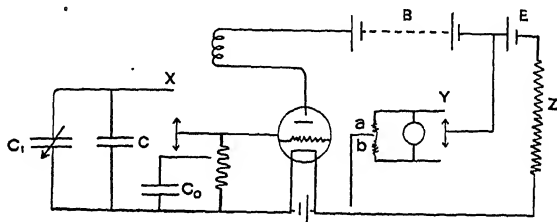
FIG. 10 (XIII *)

Modified Ultra-Micrometer Method. Considerable difficulty is caused in
the above method by fluctuations in valve emission due to low tension and
high tension battery supply. A method in which these difficulties have
been eliminated is described by Dowling and Somerville [1] in which the
capacities C and C_0 and the galvanometer connections are synchronously
interchanged by contact makers X and Y (Fig. 10 (XIII *)). The galvano-
meter shunt resistances a, b are equal, and the contact makers are ' cam-
operated ', thus ensuring good and accurately timed contact. The method
has been used with considerable success for moisture testing of various
substances, the substance being contained in a suitable condenser C_1, of
which the dial can be marked directly in moisture percentages. For many
materials (e.g. tobacco) a weighed sample is compressed by a piston electrode
in a cylindrical vessel of standard dimensions $\left(\text{cf. capacity} = \dfrac{KA}{4\pi d} \right)$.

For flour and other powders special containers are employed which
ensure even packing.

Readings are reproducible to $0 \cdot 1$ per cent of moisture—for highest
accuracy temperature corrections are necessary.

In recent years, also, some instruments for the measurement of the
dielectric constant were put on the market.

[1] U.K. Patent 337,785.

The 'Dielkometer' made by Messrs. Haardt & Co., Düsseldorf, and designed by Professor Ebert, [1, 2, 3, 4] is intended for technical measurements. It is based on the 'Heterodyne Beat Method' (see Fig. 7 (XIII *)); the adjustment is made with the aid of a headphone, the point of inaudibility being the mark of adjustment.

The 'Beha' meter is a technical instrument of the firm of Beck &
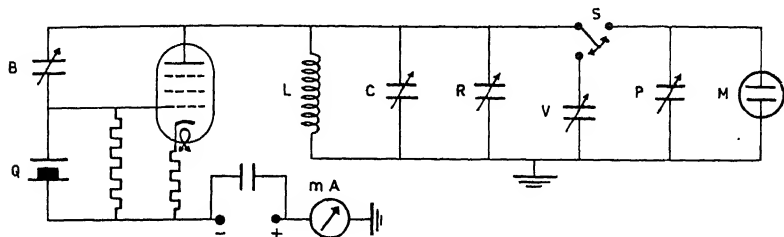
FIG. 11 (XIII *)

Hartman, Copenhagen, and specially intended for the rough measurement of the moisture in grains.

An apparatus allowing very accurate scientific measurements, but which is also supplied in a simpler, cheaper form for technical measurements, was designed by P. Cohen Henriquez, [5, 6, 7, 8] and is supplied by Messrs. Kipp & Zonen, Delft (Holland). The electric scheme (simplified) is represented in Fig. 11 (XIII *).
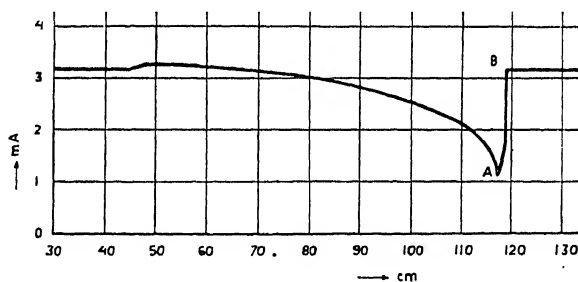
FIG. 12 (XIII *)

The principle of the working of the apparatus is based on the resonance of the quartz crystal Q with the LC circuit, in which also the measuring cell M is inserted.

The plate current of the pentode is read off on the milliammeter. This plate current depends in a peculiar way upon the capacity in the LC circuit, viz. in the way as represented in Fig. 12 (XIII *).

Starting from a small capacity and increasing this, the plate current

[1] Ebert and Waldschmidt, *Z. phys. Chem.*, Bodenstein Festband, 1931, 101.
[2] Ebert, *Angew. Ch.*, 1934, *47*, 305.   [3] Ebert, *Chemische Fabrik*, 1934, *7*, 180.
[4] Ebert, *Forschungen und Fortschritte*, 1934 (April), *10*, 20.
[5] P. Cohen Henriquez, *Physica*, 1933, *1*, 41.
[6] P. Cohen Henriquez, *Rec. trav. Chim.*, 1935, *54*, 327.
[7] P. Cohen Henriquez and W. Renaud, *Physica*, 1935, *2*, 425, 429.
[8] P. Cohen Henriquez, *Physica*, 1935, *2*, 434.

will fall gradually (gradually the system begins to generate) until it reaches a minimum ; a further rise of the capacity causes the plate current to increase very sharply. At the right of the minimum—in the critical region in which the frequency is quite close to the self ('eigen') frequency of the quartz—the slope of the curve is so steep as to admit of an accuracy of adjustment which is greater than 0·001 cm., in spite of the fact that only a very rough indicating instrument is used. The apparatus is provided with a built-in high tension apparatus and can directly be connected to the A.C. supply (110, 127 or 220 volts). Changes in the tension of the supply have practically no influence on the adjustment.

The quartz crystal is interchangeable, so that measurements can also be made at greater or smaller wavelengths by inserting other crystals.

In Fig. 11 (XIII *) M represents the measuring cell, i.e. the condenser containing the material to be tested. P is a precision condenser for measuring the effect which occurs, if the measuring cell is filled (respectively, if a material of a known dielectric constant is replaced by one, the dielectric constant of which has to be measured). C is a condenser 250 cm.

In case of very accurate measurements, it is of importance to correct the influence of small variations which take place in the valve and which may cause a small inconstancy of the adjustment. For this purpose, the capacity of (P + M) can be compared with that of a verification-condenser, V. On commencing an experiment, the capacity of (P + M) is made equal to the capacity of V. The precision switch S enables to change over from (P + M) to V. At the end of the experiment we switch over again to V. If the reading on the milliammeter has remained constant, the generator has not deviated. If, on the contrary, there has been some deviation, this is corrected by means of the small auxiliary 'readjustment-condenser' R, after which we switch over again to (P + M) and definitely adjust P. Of course the construction of the switch S must be very accurate.

The precision condenser P consists of a pin, over which a hollow screw can be moved up and down. The capacity of this condenser is 5 cm. The calibration curve is, for an important part at least, strictly linear with an accuracy of 0·001 cm. Each scale division corresponds to a capacity of 0·001 cm.

The measuring cell *for liquids* (a simplified drawing of which is shown in Fig. 13 (XIII *), which is normally supplied with the apparatus, has a capacity of about 10 cm. and a volume of about 1 ml. It consists of two glass tubes concentrically adjusted, leaving open an annular space with inlet and outlet channels. The inner tube is platinized on the outside, the outer tube on the inside. The two thin platinum layers form the coatings of the condenser ; the distance between them is very small. The condenser is filled at A, while B is kept closed. It may be emptied by blowing in dry air at C.

The measuring-cell for liquids is placed in a Dewar vessel serving as a thermostat. The Dewar vessel may be filled with suitable liquids. The heat capacity of the bath liquid as compared with that of the liquid in the condenser is such that in normal cases (working at about room temperature) regulation of temperature will be superfluous. For working at higher temperatures a heating element is built in.

Measuring-cells for liquids having a capacity of 1 cm. and of 0·2 cm. are also supplied. The condensers can very easily be interchanged and can be mounted very rigidly.

For solids and for powdered and fibrous substances condensers have been constructed which compress the material under investigation to a definite, accurately fixed volume. Fig. 14 (XIII *) illustrates one of the shapes in which the condenser for solids is executed. The three standard patterns have capacities of 10, 1 and 0·1 cm. They can also be used for the measurement of liquids and of substances of a buttery consistence.

It is quite clear that apart from the precision condenser P, measurements
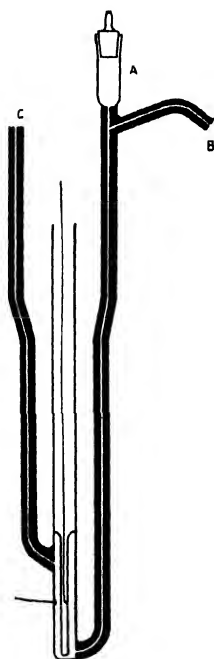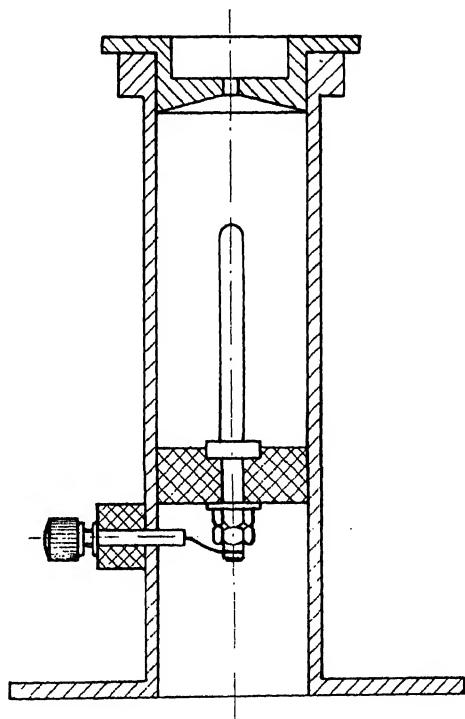
FIG. 13 (XIII *)   FIG. 14 (XIII *)

can also be made with C and V of 250 and 100 cm. Both are provided with a scale with vernier.

The generating is hindered by substances containing much moisture, the accuracy of the measurements suffering from this. To eliminate this trouble as much as possible, the regeneration can be increased by means of the regenerative condenser B.

At the right-hand side the instrument is provided with means for connecting measuring cells, condensers, &c., which, for some reason or other, have to be used outside the apparatus. The apparatus is shown in Fig. 15 (XIII *).

On the right-hand side of the apparatus are the scales with rough- and

PHYSICO-CHEMICAL METHODS

fine-adjustment buttons for the condensers. In the middle at the top is the milliameter by means of which the adjustments take place. Below this is the button of the appositional condenser on the left-hand side of which again there is the switch button. Entirely on the left is the button and the scale division of the precision-condenser. On top of the apparatus the hopper of the liquid condenser is seen to stick out. Behind this is
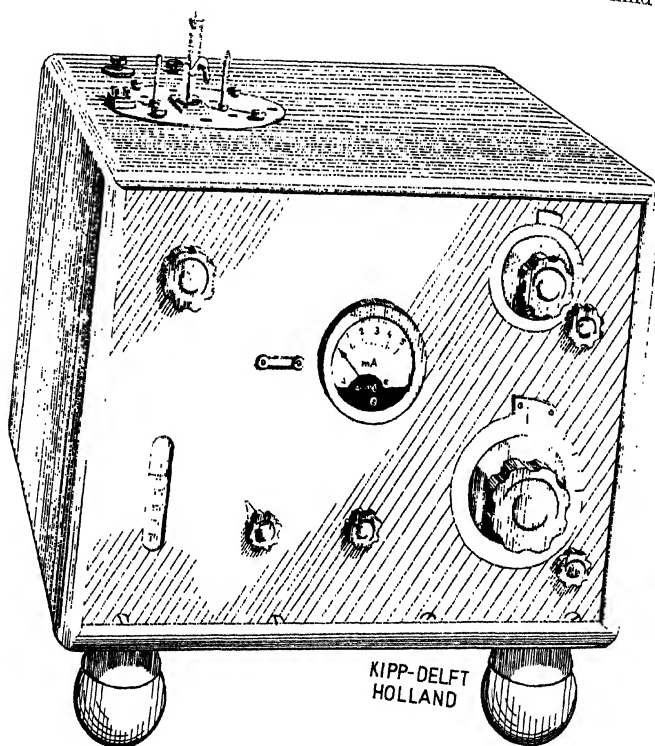
FIG. 15 (XIII *)

the hopper for the back-coupling. The apparatus is mounted on four tennis balls in order to prevent possible shocks.

In the simplified apparatus for technical measurements, named 'Elmometer', the condensers, the precision-condenser, the switch and the Dewar-vessel are omitted. Measurements can be made with a condenser of 25 cm. and a condenser of 100 cm. An accuracy of 0·01 cm. can be obtained.

The apparatus is very compact (32·5 × 26 × 13·5 cm.) and adapted to rough handling. It is also possible to make comparative measurements

of dielectric losses with the apparatus in Fig. 15 (XIII *), which are very important for testing insulating materials.

The minimum of the plate current (see Fig. 12 (XIII *)) is dependent upon the dielectric losses, being lowest with small losses. So this minimum provides a means of measuring these losses.

In this case it may be appropriate to use an indication-instrument with a greater accuracy than the milliammeter. Means are provided to connect very easily a sensitive instrument in series with the milliammeter.

Vibrations can be performed with the aid of the instrument by using instead of the ordinary measuring-cell a vibration-cell in series with a condenser.

The methods described above will not do for measuring in the case of very short waves. In these cases we had better proceed according to the method of *Drude* (see Fig. 16 (XIII *)).

In ring 1 with the Lecher wires L_1 and L_2, stationary waves are generated by means of induction with a Tesla apparatus. At point A, for example, a node is produced ; by means of a Geissler tube with both contacts moving along the Lecher wires, the places of the loops can be ascertained and con-
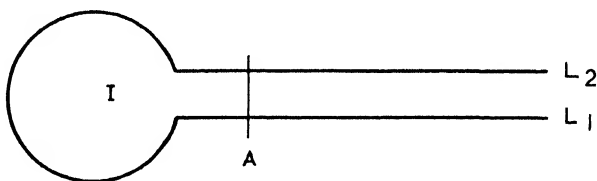
FIG. 16 (XIII *)

sequently the wave-length can be determined. The Lecher wires are inserted into the liquid that is to be examined. The dielectrical constant is computed from $\varepsilon = \dfrac{\lambda_0 2}{\lambda 2}$, where $\lambda_0 =$ wave-length in air and $\lambda =$ the wave-length in the examined medium.

Worthy of mention is a method applied in 1930 by *Goldammer* and *Sack* for wave-lengths of ± 1 M.[1, 2] The short waves are obtained according to the method of *Barkhausen-Kurz*.[3] A special Phillips Z-lamp was used. The grid is positive in regard to the filament, the anode is negative. See Fig. 17 (XIII *).

The electrons vibrate at both sides of the grid. By means of the wires attached to the grid and the anode short-circuited with condenser C_1, the vibration is transmitted to circuit II, which is tuned. Circuit II again transmits the vibration to circuit III. The measuring-cell M is soldered to two Lecher wires. The movable short-circuit condenser C (the place of which can be read by means of a measuring-staff) is shifted until the ring is in resonance (criterion : reading of a mirror-galvanometer).

Through the filling of M with various liquids of known dielectrical constant a calibration is obtained.

A method which is by no means suitable for general application, but,

[1] Goldammer and Sack, *Phys. Zeit.*, 1930, *31*, 224.
[2] Wechsung, *Zeitschr. f. Hochfrequenztechnik*, 1928, *32*, 58.
[3] Barkhausen, *Elektronenrohre.*

on principle, very interesting, is the 'molecular "ray"' method of *Wrede* and *Estermann*.[1, 2, 3]

No great accuracy is to be reached with this method; it is useful, how-
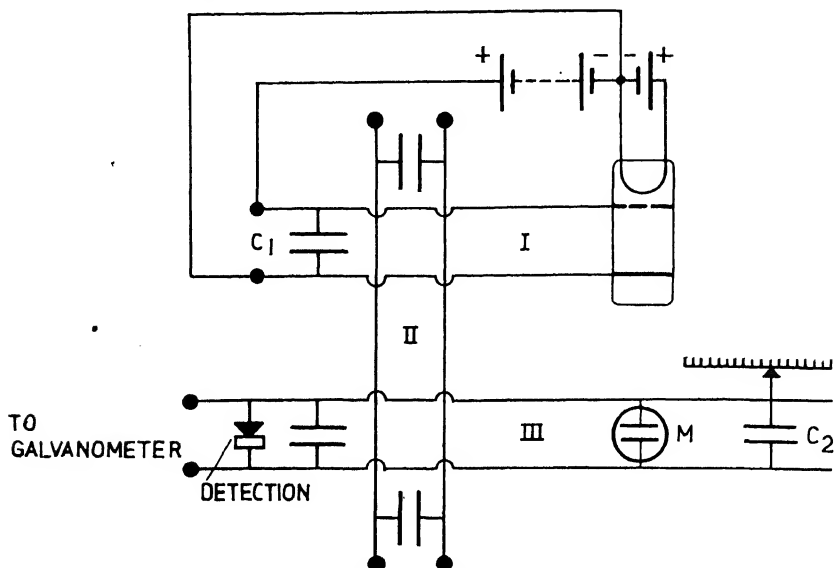
FIG. 17 (XIII *)

ever, for substances with exceptionally large dipole moment, like the alkali salts, which, owing to their electrolytic dissociability, their high boiling-point and their insolubility in ordinary organic solvents, render measuring according to other methods impossible.

APPLICATIONS OF DIELECTRIC CONSTANT MEASUREMENTS

Liquids (Non-electrolytes). If the polarization formulae given at the beginning of Chapter XIII * are applied in the case of dipole liquids, it appears that they do not hold good at all. When dissolving a small quantity of a dipole substance in a dipole-free liquid, the formula can indeed be applied to this solution without too serious errors (though small differences occur even then). In the case, however, of a greater concentration, the formula no longer holds good. The additivity of the polarizations, *a priori* to be expected when using the formula, will not hold good at all. Fig. 18 (XIII *) makes this clear.

If a dipole substance 2 is dissolved in a non-polar liquid 1, the line ¯AC is the calculated one [4] and the line AB that which is actually found.

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[1] Wrede and Estermann, *Z. phys. chem.*, 1928, B, *1*, 134-61; 1928, *2*, 287; 1933, *20*, 195.

[2] Wrede and Estermann, *Z. Physik.*, 1927, *44*, 26.

[3] Grignard, cited under Grignard, page 503.

[4] If use is made of the dipole moment measured in a diluted solution, using the additivity formula $P_{12} = f_1 P_1 + f_2 P_2$ whereby f_1 and f_2 represent the molar concentrations, P_1 and P_2 the molar polarizations of the two substances and P_{12} the molar polarization of the mixture.

On the other hand, if two dipole liquids 1 and 2 are mixed, one with a dielectric constant of ε_1 in a pure state, the other with a dielectric constant of ε_2 in a pure state, then the P_{12}-line calculated with the values ε_1 and ε_2 for all proportions of mixture of 1 and 2 is a straight one, but in reality it is a curved line between E and C.

Hitherto a satisfactory explanation for these deviations has not been given. *Van Arkel and Snoek* [1, 2] have tried to give an empirical formula for the mutual influence of the dipoles; this formula, however, does not explain the anomalies observed by *Müller* [3, 4], with dilute solutions in several non-polar solvents. On the other hand, the formula of *Müller* for the anomalies in dilute solutions does not explain the anomalies in concentrated solutions.[5] Another empirical formula given by *P. Cohen Henriquez*,[6] universally applicable in all cases dealing with liquids smaller than 30, gives for most cases satisfactory agreement with experimental data.
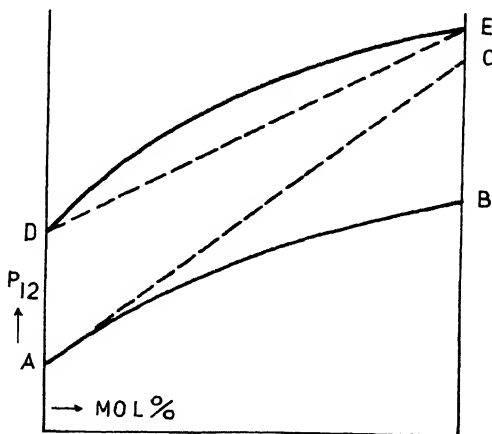
The formula for the molecular polarization of *Clausius-Mosotti*,

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d}$$

was replaced by $\quad\quad P = \dfrac{(\varepsilon - 1)(\varepsilon + 4)}{\delta\varepsilon + 7} \cdot \dfrac{M}{d} \quad . \quad . \quad . \quad . \quad (5)$

Reaction Control, Association, &c. If a reaction of two substances takes place, the substance which arises will generally possess a polarization differing from the sum of the polarizations of the initial substances. During the reaction the dielectric constant will change. So, the dielectric constant makes it possible to ascertain whether a reaction occurs, which is not always possible by chemical, or other physical methods (associa-

FIG. 18 (XIII *)

[1] van Arkel and Snoek, *Phys. Zeit.*, 1934, *35*, 187.

[2] Snoek, *Phys. Zeit.*, 1934, *35*, 196.

[3] Horst Müller, *Phys. Zeit.*, 1932, *33*, 731; 1933, *34*, 689; 1937, *38*, 283.

[4] Horst Müller and Mortier, *Phys. Zeit.*, 1935, *36*, 371.

[5] For these subjects, see also the publications of *Le Fèvre*,* *Jenkins*,† *Sugden*,‡ *Raman* and *Krishnan*.§

[6] P. Cohen Henriquez, *Rec. trav. Chim.*, 1935, *54*, 574.

* G. C. Le Fèvre and R. W. Le Fèvre, *J. Chem. Soc.*, 1935, 1748.

† Jenkins, *J. Chem. Soc.*, 1934, 481.

‡ Sugden, *Nature*, 1934, *133*, 415.

§ Raman and Krishnan, *Proc. Roy. Soc.*, 1928, *117* A, 589.

tions, labile compounds), to follow continuously the course of the reaction in a simple way and sometimes to get an idea of the nature of the reaction products. Interesting cases were reported by *Briegleb, Kambeitz, Le Fèvre, Earp, Glasstone, Pestemer, Fruhwirth.*[1, 2, 3, 4, 5, 6]

We may also mention the work of *Ulich, Nespital,* and *Hertel.*[7, 8, 9, 10]

The last-mentioned investigations were chiefly devoted to the formation of complex compounds between non-polar metal halides and organic substances, which complexes are marked by extremely large dipole moments, much larger than the moment of the organic substances in question. Below we will come back to this question (see also Table 3).

If the class of investigations with which we are dealing here are performed in dilute solutions with low dielectric constants (<4), the formulae of *Clausius-Mosotti* and *Debye* (2), (3), (4) can be used without serious errors. As already said, however, they do not hold good in solutions with high dielectric constants (>4).

In that case the formula (5) given above enables us to draw interesting conclusions from the reciprocal action of the molecules in a liquid state,
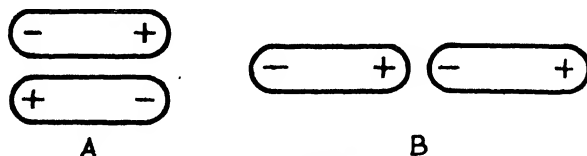
FIG. 19 (XIII *)

for we know that this formula enables us to describe more or less the ' normal ' behaviour of the substances. Hence, important deviations point to something particular.

If we mix, for example, alcohol with carbon tetrachloride or benzene, if we plot the polarizations of the mixtures (as calculated with the aid of formula (5)) against the concentration, a line is obtained which for small concentrations of alcohol deviates very strongly from a straight one. The explanation is that the alcohol molecules have a strong disposition towards association due to the dipoles of the OH groups being situated close to the periphery.

Association can proceed as shown under A and under B in Fig. 19 (XIII *). In the case of association as per A, the polarization decreases, in the case of B the polarization increases (dipole moment twice as large, so the polarization per double-molecule four times as large, number of molecules twice as small). Sometimes A as well as B takes place.

[1] Briegleb and Kambeitz, *Z. phys. Chem.*, 1934 (B), *25*, 251.
[2] Briegleb, *Z. phys. Chem.*, 1936 (B), *31*, 58.
[3] C. Le Fèvre and R. W. Le Fèvre, *J. Chem. Soc.*, 1936, 487.
[4] R. W. Le Fèvre and P. Russel, *J. Chem. Soc.*, 1936, 491.
[5] Earp and Glasstone, *J. Chem. Soc.*, 1935, 1709.
[6] Pestemer und Fruhwirth, *Wiener Akad. Wiss. Sitzungsber. d. Mathem-naturw. Klasse*, 1937, *2* B, 146 Band, Heft 2, pp. 150, &c.
[7] Ulich and Nespital, *Z. Elektrochem.*, 1931, *37*, 559.
[8] Ulich and Nespital, *Z. angew. Chem.*, 1931, *44*, 750.
[9] Nespital, *Z. phys. Chem.*, 1932 (B), *16*, 153.
[10] Ulich, Hertel, and Nespital, *Z. phys. Chem.*, 1932 (B), *17*, 21.

Fig. 20 (XIII *) represents a case in which a dipole substance is mixed with a dipole-free liquid, association taking place with a small concentration as per B and, with larger concentrations, the compound partly associating forming larger dipole-free aggregates of molecules as per A. AB is the line as can be calculated, with-out taking into considera-tion the association.

In Fig. 21 (XIII *) the case is represented in which two substances 1 and 2 are mixed, which combine to form a compound in the ratio 1 : 2 which has a larger dipole moment than 1 or 2. If this compound is not dissociated, two straight lines AC and CB are ob-tained ; if it is dissociated, the curve AB is obtained. The straight line AB is the one calculated without con-sidering the formation of a compound.
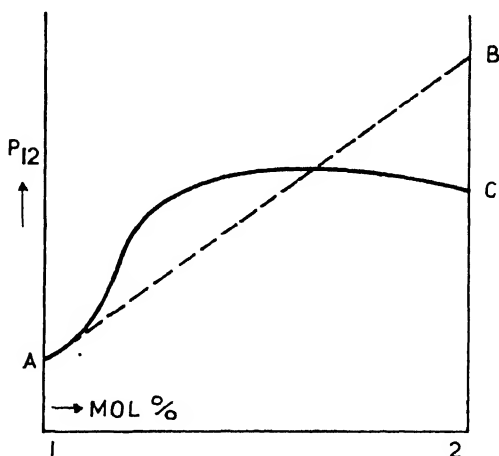
FIG. 20 (XIII *)

Control of Purity, Identification. The dielectric constant allows in many cases of a very sharp control of the purity of liquids, and is an important physical constant for the identification of substances or mixtures of substances. This is par-ticularly the case, if one has to detect the contamination of a substance by another substance, which has a much higher dielectric constant. For instance, with the aid of the above-described apparatus it is possible to detect the contamination of benzene by water (dielectric constant = 80, dipole moment = 1·8 D) with an accuracy of 0·001 per cent.

In a great variety of cases the dielectric constant allows of a much better control than the refractive index.

FIG. 21 (XIII *)

Control of Distillations. Dielectric constant measurements, carried out continuously, will give valuable information as to the process of dis-tillations.

Fig. 22 (XIII *) represents the line which would be obtained by plotting
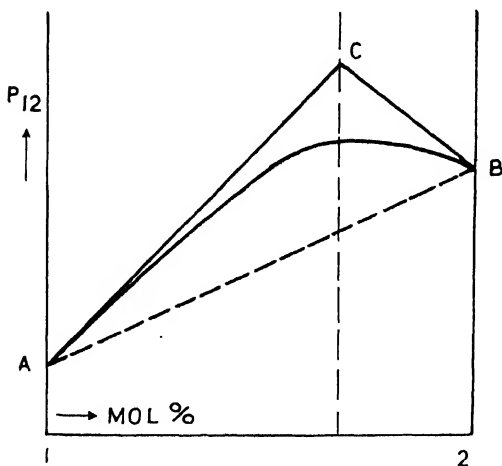
the volume of the distillate against the dielectric constant in the case of a distillation being effected of a ternary mixture, for the larger part consisting of benzene mixed with small volumes of acetone and nitrobenzene.
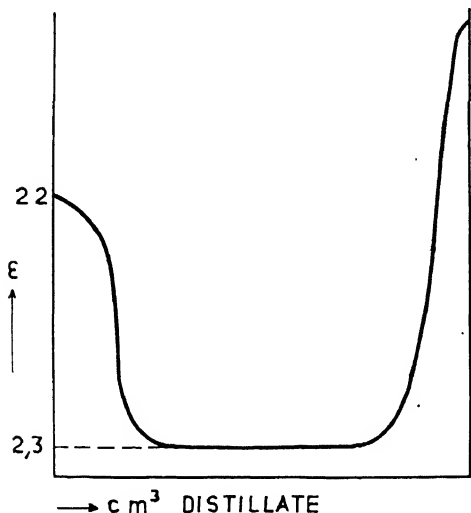
Control in Manufacture. In the manufacture of many industrial products it may be of importance to stop the manufacturing process automatically as soon as the product has reached a certain composition and has thus obtained a certain dielectric constant. This control can be carried out continuously by means of an apparatus for dielectric constant measurement. The apparatus possesses the advantage that signal appliances or other automatic devices can easily be operated by it, it being very easy to amplify the plate current to each desired magnitude.

Solids

(a) *Dielectric Constant of Powders, Granular and Fibrous Substances.* The practical importance of these measurements chiefly concerns the measurement of the moisture content. In the foregoing, condensers were already described which are suitable for this purpose. Theoretical formulae for such measurements cannot be given. For each substance it is necessary to make once a calibration curve and to work always under similar conditions, measuring a given quantity of material in a condenser of given size and volume. When taking these precautions into account, in many cases an accuracy of 0·1 per cent of moisture or even more can be attained (e.g. in flour, artificial silk, sugar, tobacco, coal, &c., &c.).

(b) *Substances being Solid at Normal Temperature.* If one wants to know the dielectric constant of the solid itself, the method described above cannot be applied, of course. Then proceed as follows.

Make a series of liquid mixtures of different dielectric constant. Put one of the mixtures into a condenser for solids as described and ascertain whether the capacity decreases or increases, when bringing a quantity of the solid into the liquid. Continue repeating these tests until a liquid mixture has been found, the dielectric constant of which is equal to that of the solid. In this case the capacity does not change or changes a very little only, when the solid is put into the liquid mixture.

(c) *Substances being Liquid or Gaseous at Normal Temperature.* These substances must be solidified in the condenser, which involves a number of difficulties. First of all, air is liberated during the freezing process so

FIG. 22 (XIII *)

that it is necessary previously to free the liquid from air to the highest possible degree. However, also in case of the substance having been thoroughly freed from air, spaces and clefts may arise during freezing. Furthermore, a certain preferred direction may occur during the crystallizing.

These three circumstances make it difficult to get a homogeneous product which, however, is not strictly necessary in many cases. The dielectric constant measurements on solids are very interesting in many respects. First, they are of value in the elucidation of the mobility of the molecules, the atoms or groups of atoms within the crystal. On a superficial view, it could be expected that the molecules within the crystal are fixed in such a way that they are not allowed to move freely in the electric field, and consequently that the share in the polarization caused by the orientation of the dipoles would fall off, in other words, that also dipole substances in a solid state would always have a very low dielectric constant. Now it appears that this is not always the case. Of course, for the molecules (or groups) within a crystal it is more difficult to move than in a liquid, but in many cases there is no question of their being completely hindered from moving. For example, ice has at 0° a very high dielectric constant, if this is measured in an alternating field with a frequency lower than 10^4 Hertz.[1] At higher frequencies the dielectric constant decreases very strongly. This behaviour indicates that the movement of the molecules within the crystal is impeded to such a degree that they are no longer allowed to follow frequencies of, for example, 10^5. At lower temperatures this impediment increases strongly, so that the decrease of the dielectric constant begins already at much lower frequencies.

In experiments with solid hydrogen-halides it has been found that the dielectric constant shows large jumps at certain temperatures. With HCl a 'transition point' was found at 98° K., with HBr three such transition points were found, viz. at 89°, 113° and 117° K., and with HI two of them, viz. at 70° and at 126° K. For an explanation of this we refer to the original literature.[2]

Smith and *McNeight*[3] found for solid methyl-alcohol with frequencies of 5,000–50,000 Hertz high D.C. values; for tertiary butyl alcohol and octyl alcohol he did *not*. He concludes from it that the entire CH_3OH molecule rotates in the lattice and that the OH group doesn't do so individually. *Higasi*[4] found in the solidifying of cetyl alcohol a sudden increase of the D.C. frequency of 3,000 kilocycles. With a further decrease of the temperature the D.C. value goes through a maximum and falls very steeply 20° below the point of solidification. One is inclined to interpret this in such a way as would make the OH group seem to be movable in the crystal lattice of cetyl alcohol. Confirmation of similar measurements, however, must be awaited.

Similar observations were made by *Piekara* with solid oleic acid.[5] Particularly remarkable is the behaviour of the solid *Seignette salt*. Between

[1] Murphy, Bell Telephone System's Technical Publications, Monograph B, 1935, 832.
[2] Frenkel, Todes and Isimailow, *Acta Physicochimica U.R.S.S.*, 1935, *1*, 97.
[3] Smyth and McNeight, *J. Amer. Chem. Soc.*, 1936, *58*, 1597.
[4] Higasi, *Bull. Chem. Soc. Japan*, 1937, *12*, 326.
[5] *Piekara, Phys. Zeit.*, 1936, *37*, 624.

— 20° and — 25° this shows a region in which there is no question of a constant value for the D.C., the value is then quite dependent on the field. If the field stops working, the polarization does not quite disappear; analogous to ferromagnetic substances in which a residual magnetic polarization remains, in the *Seignette salt* a residual electric polarization is left.

CONDUCTING SOLUTIONS

The measurement of the D.C. of electrolytes involves many more difficulties than the D.C. measurement of non-conducting substances. In the first place the accuracy of adjustment is very unfavourably affected by the conductibility, in the second place there are always the combined influences of variations of capacity and resistance to be considered with each measurement. The influence of the change of resistance is therefore to be compensated. The difficulties involved with these measurements are illustrated by the fact that it has been disputed for years whether dilute solutions of electrolytes possess a D.C. larger or smaller than that of water, this point being of importance for the verifying of the *Debye-*, *Hückel-*, and *Falkenhagen* theory of dilute solutions. It is not very long ago that this dispute was settled in favour of the first-mentioned conception.

In order to eliminate, when measuring, the influence of the changes of resistance, one may, on principle, proceed as follows (see Fig. 23 (XIII *)).
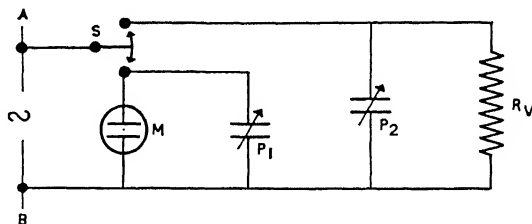
FIG. 23 (XIII *)

In the high frequency circuit there can be taken up either : (the measuring-cell M + the precision condenser P_1) or : (the resistance ' without capacity ' R_v + the precision condenser P_2). The resistance R_v is equalled to the resistance of the measuring-cell M and the capacity of P_2 is equalled to the capacities of (the measuring-cell + the capacity of P_1). When switching over from one combination to the other, the adjustment must remain the same. (*N.B.*—In what way the adjustment takes place has been quite left out of account here.)

Let a solution 1 in the measuring-cell be replaced by a solution 2, causing a change in capacity of Δ C, then it may occur that, in order to get again a suitable adjustment in the part of the apparatus to the left of A–B (Fig. 23 (XIII *)), alterations will have to be made (e.g. the enlargement of the back-coupling).

Hence, if we adjust again by means of A, three influences are to be compensated with this condenser, viz. (1) the capacity variation of the measuring-cell M (ΔC_M), (2) the influence of the change of resistance of

the measuring-cell (Infl. ΔR_M), and (3) the influence of the changes in the rest of the apparatus. After having again adjusted by means of P_1, one switches over on $(P_2 + R_v)$. R_v is made equal again to R_M, readjustment takes place by means of P_2.

Let the capacity variation of P_1 be : ΔC_1, and of P_2 : ΔC_2, then :

$$\Delta C_1 = \Delta C_M + \text{Infl. } \Delta R_v + \text{other influences}$$
$$\Delta C_2 = \qquad\quad \text{Infl. } \Delta R_v + \text{other influences}$$

subtract
_____

$$\overline{\Delta C_1 - \Delta C_2 = \Delta C_M}$$

The great difficulty is to construct a resistance R_v which can be regulated in such a way that the capacity does not change.

Mazée [1] has tried to do this as follows :

He employed two short pieces of platinum wire, piercing through the glass of a vessel, one at the bottom and the other at the top. A rough regulation of the resistance can be obtained by filling the vessel with liquids of various conductivity. A more accurate regulation is possible through the moving up and down of the platinum top wire by means of a micrometer screw. The slight capacity variation caused by this moving up and down and by the filling of the vessel with variously concentrated liquids is to be eliminated by the making of correction curves. The correction curves are made through comparison with so-called ' non-capacitive and non-self-inductive ' resistances manufactured by coating porcelain cylinders with very thin layers of metal. *Mazée* applied an improved method of resonance.

For these subjects consult also the work of *Graffunder, Weber, Yesewski,* and *Kamechi* [2, 3, 4, 5, 6].

[1] *Mazée,* Thesis, 1935, Amsterdam; *Phys. Zeit.,* 1935, *36,* 177.

[2] Graffunder und Weber, *Zeit. Phys.,* 1930, *65,* 723.

[3] Graffunder und Weber, *An. Phys.,* 1931, *9,* 890.

[4] Graffunder, *An. Phys.,* 1934, *19,* 689.

[5] Tenewski, *Phys. Zeit.,* 1933, *34,* 88.

[6] Tenewski and Kamecki, *Phys. Zeit.,* 1933, *34,* 561.

SECTION 2 : DIPOLE MEASUREMENTS

We have already mentioned the formula :

$$P = {}_E P + {}_A P + {}_O P \qquad . \qquad . \qquad . \qquad . \quad (1).$$

${}_A P$ is small and is mostly neglected. P is a function of the dielectrical constant. ${}_E P$ is a similar function of the refractive index, in which ε has been replaced by n^2 (see formulae (2) and (3)).

Thus for a gas the following equation holds good :

$$\frac{4\pi N . r^2}{9kT} = \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \frac{M}{d} \qquad . \qquad . \qquad . \quad (6)$$

Measuring ε and π, r can be calculated.

It has already been mentioned that on inserting the formulae of *Clausius-Mosotti* and *Debye* for P, ${}_E P$, and ${}_O P$, formula (3), strictly speaking, only holds good for gases, that the deviations in dilute solutions are appreciable, but not very large, while in a more concentrated solution we have to manage with empirical formulae (see formula (5)).

The dipole measurement on gases, though from a theoretical point of view the most correct one, is, however, seldom applied owing to the technical difficulties of measuring. The method of dilute solutions is the one that is commonly used.

As has been said, by means of this method the dipole substance is dissolved in a dipoleless solvent. For the calculations of the dipole-moment one has only to measure :

(1) the difference in dielectrical constant between the dilute solution of the dipole substance and the dipoleless solvent : $\Delta \varepsilon$;

(2) the same difference for the refractive index : Δn.

Making use of the postulate of the additivity of the polarizations :

$$P_{12} = f_1 P_1 + f_2 P_2 = f_{1E} P_1 + f_{2E} P_2 + f_{2O} P_2 = {}_E P_{12} + f_{2O} P_2. \qquad (7)$$

holds good for the solution (from formula 3), in which

$P_{12} =$ mol. pol. for the mixture

f_1 and $f_2 =$ mol. parts of solvent 1 and dipole substance 2

$P_1 =$ mol. pol. solvent

$P_2 =$ mol. pol. dipole-substance

${}_E P_{12} =$ mol. refraction for the mixture

If we combine this with the formulas (2), (3), and (4), we get :

$$f_2 \frac{4\pi N r^2}{gkT} = \left(\frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} - \frac{n_{12}^2 - 1}{n_{12}^2 + 2} \right) \frac{M_{12}}{d_{12}} \qquad . \qquad . \quad (8)$$

in which

$\varepsilon_{12} =$ diel. const. of the mixture

$n_{12} =$ refractive index of the mixture

$M_{12} =$ mean molar weight

$d_{12} =$ density

If we work this out and use a number of simplifications which are admitted, thanks to the small concentration of the dipole substance, made possible by the use of an accurate apparatus, the following simple formula is obtained for the calculation of the dipole moment in dilute solutions : [1]

$$_0P = 6.18\frac{r'}{T} \times 10^3 = \left(a\frac{\Delta\varepsilon}{k_2} \mp b\frac{\Delta n}{k_2}\right)M_2 \tag{9}$$

in which a and b are constants dependent on the solvent and within fairly wide limits (10°) practically independent on the *temperature*, k_2 = part *by weight* [2] of the dipole substance.[2] M_2 = molecular weight of the dipole substance. For measurements in benzene solutions at a temperature between 15° and 25°, e.g. :

$$_0P = 6.18\frac{r}{T} \times 10^3 = 0.1893\frac{\Delta\varepsilon}{k_2} - 0.567\frac{\Delta n}{k_2} \tag{10}$$

holds good.

It is evident that on making use of the empirical formula (5) already given, calculations can be linked up with the results of the measurements obtained in the case of solutions which are much more concentrated.[3]

APPLICATION OF DIPOLE MEASUREMENTS

Direction and Magnitude of the Dipole Moment. In order to know with which atom the negative side of the dipole and with which atom the positive side of the dipole is situated, the following rough rule may be used, which is often—*but not always*—valid : The tendency of an element to be negative is the greater, the more it is situated at the right-hand side and at the top of the periodic system. From this rule it follows :

(1) The negative side of the dipole between two atoms of elements occurring in the same horizontal row of the periodic system lies with the element which is the most to the right in this row.

(2) The negative side of the dipole between two atoms of elements occurring in the same vertical column of the periodic system lies with the element which is topmost in this column.

The above-mentioned rule is illustrated by Table 1 (see also Table 6).

[1] The dipole moment r is expressed in Debye-units $1D = 10^{-18}$ electrostatical units.

[2] If one holds to the justness of the formula of *Clausius-Mosotti*, we have :

$$a = \frac{3}{(n_1^2 + 2)^2} \text{ and } b = \frac{6n_1}{(n_1^2 + 2)^2}$$

Starting with the empirical formula (2) we have :

$$a = \frac{8n_1^4 + 14n_1^2 + 53}{(8n_1^2 + 7)^2}; \quad b = \frac{2n(8n_1^4 + 14n_1^2 + 53)}{(8n_1^2 + 7)^2}$$

It goes without saying that, also in dilute solutions, different results are obtained, when starting from the empirical formula (5) instead of from the formula of *Clausius-Mosotti*. In order to be able to compare a dipole moment computed by means of the empirical formula with a dipole moment computed by means of the formula of Clausius-Mosotti in benzene solution, the former is to be multiplied by 0.91.

[3] Naturally, in that case the simple formula (9) does not hold good, the expression for the polarization must be inserted in formula (7).

So we see that in the series HCl, HBr, HI the moment decreases, for the tendency to be negative of the halogens decrease also in this series.[1]

TABLE 1

Subst.	r	Subst.	r	Subst.	r	Subst.	r	Subst.	r
HCl	1·2	NH_3	1·5	H_2O	1·8	$S(C_6H_5)_2$	1·47	$P(C_6H_5)_3$	1·45
HBr	1·0	PH_3	0·6	H_2S	1·2	$Se(C_6H_5)_2$	1·38	$As(C_6H_5)_3$	1·07
HI	0·6	AsH_3	0			$Te(C_6H_5)_2$	1·13	$Sb(C_6H_5)_3$	0·57
								$Bi(C_6H_5)_3$	0

Studies on Structure. The studies on structure by means of dipole measurements are based on the following postulates :

(1) A group X connected with a hydrocarbon-residue R (which may or may not be substituted) has a characteristic moment that is independent of the nature of R.

(2) The moments of the substituents may be regarded as vectors and a molecule containing several substituents has a moment which is the resultant of the partial moments, computed by the rules of vector addition.

(3) The moment C—H is equal to zero.

Postulate 3 yields the fewest difficulties, the moment C—H cannot be determined (all aliphatic and aromatic hydrocarbons which are not substituted, are dipoleless owing to their symmetrical structure) ; it is therefore supposed to be equal to zero, all other moment values thus being virtually measured ' relative with respect to the C—H moment '.

FIG. 24 (XIII *)

The postulates 1 and 2 have qualitative validity only, in a sufficient degree, however, to make many studies on structure possible.

The deviations found from these rules are connected with the mutual influencing of the substituents and hence, for this very reason, are sometimes most interesting.

Below we shall further return to this last-mentioned fact.

An example of vectorial additivity is given in Fig. 24 (XIII *).

The approximate values [1] for a great number of groups are given in Table 2 (when the positive side of the dipole is directed towards the substituent, the moment is indicated as negative).

Between the moment values for the groups substituted in an aromatic and an aliphatic residue, there is sometimes a rather important difference as is shown in this table.

From the postulate of the vectorial additivity it follows that in

[1] See the table of dipole moments in ' Dipole Moments ', a General Discussion, *Trans. Far. Soc.*, Sept. 1934. Reprint published by Gurney & Jackson, London.
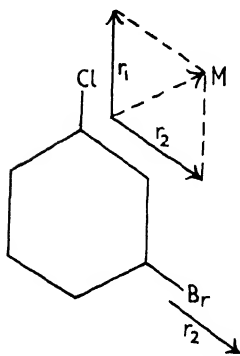
TABLE 2

Axial-symmetrical			Non-axial-symmetrical		
Substituent	r in D		Substituent	r in D	
	Al.	Ar.		Al.	Ar.
$-CH_3$	0	-0.4	$-OH$	1.7	1.7
$-F$	1.8	1.6	$-OCH_3$	1.3	1.2
$-Cl$	1.9	1.7	$-OC_6H_5$	1.2	1.1
$-Br$	1.8	1.7	$-SH$	1.4	1.4
$-I$	1.6	1.5	$-SC_2H_5$	1.6	—
$-NO_2$	3.2	4.0	$-SC_6H_5$	—	1.5
$>SO_2$	4.4	5.1	$-NH_2$	1.3	1.5
$>CO$	2.8	3.0	$-NO$	—	3.2
$>CS$	—	3.4	$>S=O$	—	4.1
$-CN$	3.5	3.8	$-C{<}^O_H$	2.5	2.7
$-N=C$	—	3.5	$-C{=}^O_{OH}$	(1.7 ?)	(1.7 ?)
$-N=C=S$	3.3	3.0			
$-N=C=O$	—	2.3	$-C{=}^O_{O.C_2H_5}$	1.8	1.9
	—	1.5	$-CH=CH_2$	0.4	—
$-N{<}^N_{\parallel}{}_N$			$-C{\equiv}CH$	—	0.4

symmetrically structured compounds with rigid molecules the moments neutralize one another, the total moment being zero. Thus, it is evident that, for example, CH_4, C_6H_6, $p.C_6H_4Cl_2$, and symmetrical $C_6H_3Cl_3$ must be dipoleless, which appears indeed to be the case.

In many more cases dipole measurements about the structure of molecules have been elucidatory.

Thus, it appeared that all compounds in which on one central atom more than three other atoms are attached, are absolutely symmetrical. Compounds like SiH_4, CCl_4, $SiCl_4$, $SnCl_4$, PCl_5, $SbCl_5$ are all dipoleless. They become, on the other hand, very asymmetrical as soon as they form addition compounds with other substances.

$AlCl_3$, for example, is dipoleless in carbon disulphide; in benzene, however, it has the very large moment of 5·0 D. Apparently, the $AlCl_3$ thus ' adds ' a benzene molecule, by which process the three Cl atoms, which otherwise lie in one plane (on account of which the moments neutralize one another), are drawn out from the plane. Similar phenomena occur with $BeCl_2$, BCl_3, $TiCl_4$ and $SnCl_4$, which form with some organic substances addition compounds with extremely large dipole moments (see Table 3).

Of the compounds of trivalent elements there are many with non-symmetrical 'angular' structure. NH_3, PCl_3, $AsCl_3$, and $SbCl_3$ have moments. Hence, these molecules are to be thought of as trilateral pyramids, of which the central atom is placed in the top.

An angular structure is also shown by the oxides, as also by the bivalent and most quadrivalent sulphur compounds.

TABLE 3

Complex	r	Complex	r
$BeCl_2.2(C_2H_5)_2O$ . . .	6·8	$AlBr_3.C_6H_5NO_2$	9·2
$BeBr_2.2(C_2H_5)_2O$ . . .	7·5	$AlCl_3.C_6H_5COCl$ . . .	9·0
$BCl_3.CH_3CN$	7·7	$AlCl_3.(C_6H_5)_2.CO$ . . .	8·5
$BCl_3.(C_2H_5)_2O$ . . .	6·0	$TiCl_4.C_2H_5CN$ . . .	6·0
$AlCl_3.C_6H_6$	5·0	$TiCl_4.C_6H_5CN$ . . .	6·1
$AlCl_3.C_2H_5NH_2$ . . .	6·9	$SnCl_4.(C_2H_5)_2O$ . . .	3·6
$AlCl_3.(C_2H_5)_2O$ . . .	6·5	$SnCl_4.2(CH_3)_2CO$ . .	7·7
$AlBr_3(C_2H_5)_2O$	6·5	$SnCl_4.C_6H_5CN$ . . .	7·0
$AlCl_3.C_6H_5NO_2$	9·2	$SnCl_4.2C_6H_5COCH_3$ . . .	8·7

TABLE 4

Subst.	r	Subst.	r	Subst.	r
PCl_5	0	$SiCl_4$	0	PCl_3	1·0
		$TiCl_4$	0	$AsCl_3$	2·0
$SbCl_5$	0	$SnCl_4$	0	$SbCl_3$	4·0
		SiF_4	0		
		SiH_4	0	NH_3	1·5

TABLE 5

Subst.	r
$BeCl_2$	0
BCl_2	0
$AlCl_3$	0
PCl_3	1·0
$AsCl_3$	2·0
$SbCl_3$	4·0

TABLE 7

Subst.	r
CS_2	0
CO_2	0
SO_2	1·6
SO_3	0

TABLE 6

	F	Cl	Br	I
P	—	0·9	0·6	0
As	2·65	2·15	1·6	1·0
Sb	—	3·9	3·0	1·5

The most important factors which are decisive for a symmetrical or non-symmetrical structure are :

(1) The size and the polarizability of the central atom.

(2) The size of the atoms or groups which are bound on the central atom.

(3) The number of atoms or groups which are bound on the central atom.

A non-symmetrical structure will be seen to be favoured by a *large* and *strongly polarizable* central atom and a *small number* of *small* peripheral atoms.

The above-mentioned is illustrated by the Tables 4, 5, 6, and 7.

Groups with Non-axial-symmetrical Moments. Groups like —Cl, —CH₃, —NO₂ (as is indeed to be expected from chemical evidence) appear to have moments the vector of which lies on the connecting-line C— substituent.

In the NO₂ group, for example, the moment lies, owing to the symmetrical structure, on the connecting-line C—N (Fig. 25 (XIII *)). Hence it is to be expected that the *para*-dinitrobenzene is dipoleless. The moment of an OH group, however, is composed of the moment C—O and the moment OH.
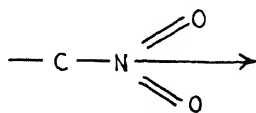
FIG. 25 (XIII *)

The valencies of the oxygen show an angle, so that the total moment does *not* lie on the connecting-line C—O (Fig. 26 (XIII *)).

The *para*-hydrobenzol is *not dipoleless*. The moments will only neutralize one another in *one* position, viz., when the H atoms are not
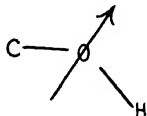
FIG. 26 (XIII *)
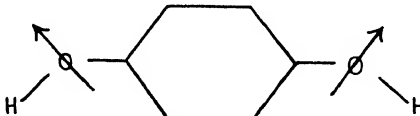
FIG. 27 (XIII *)

oppositely directed (Fig. 27 (XIII *)). The molecule, however, is not fixed in this symmetrical position, so that a total moment *does* occur. Similar groups with non-axial symmetrical moments were given in Table 2.

Naturally, with these moments, in most cases vectorial addition cannot be applied unhesitatingly.

Aromatic Compounds. Owing to the absence of a dipole moment in the *para*-substituted benzene, naphthalene and di-phenyl, the plane structure of these compounds was proved.

Cis-trans-isomerism. The prevailing notion based on chemical evidence that of the ethene-derivates two forms are possible, a *cis*- and a *trans*- form, was likewise confirmed by means of dipole measurements (Fig. 28 (XIII *)).

The *trans*- compounds, with axial symmetrical substituents proved to possess no dipole moment, the *cis*- compounds, on the other hand, *did* prove to possess dipole moments. In a few cases it could be proved by means of dipole measurements that the compound which had always been
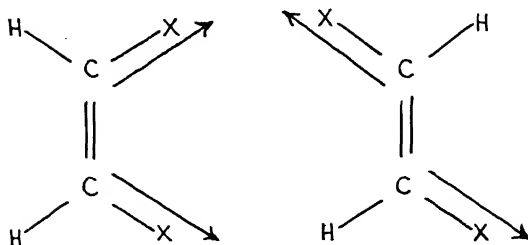
FIG. 28 (XIII *)

taken for the *cis-* form was precisely the *trans-* form, and vice versa.[1] A few examples are given in Table 8.

TABLE 8

Subst.		μ *cis*	μ *trans*
Cl	Cl	1·85	0
Br	Br	1·35	0
I	I	0·75	0
Cl	Br	1·55	0
Cl	I	1·27	0·57

An interesting case is moreover that of the thianthrenedisulfoxide (Fig. 29 (XIII *)). As has already been said, the sulfoxyde group has an 'angular' structure. On account of this two isomers are possible. The isomer with the melting-point of 246° proved to have a moment of 4·2 D,[2] the isomer with a melting-point of 279° proved to have a moment of 1·7 D. Hence, the former is apparently the *cis-* and the latter the *trans-* compound.
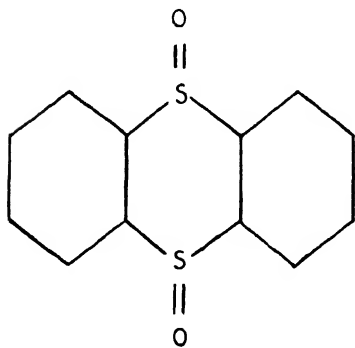
FIG. 29 (XIII *)

Some Ring Systems. From the dipolelessness of the diphenyloxide[3] it follows that the molecule is plane, while the moment of thianthrene (1·50 D) points to a non-planar-structure.

For the cyclohexane, on the ground of the hypothesis of Van 't Hoff (tetrahedron rule), two spatial models are possible.

It was now found that many 1·4 compounds of the cyclohexane are dipoleless,[4] from which it follows that the molecule must occur in the fixed 'chair position' (Fig. 30 (XIII *)). From the dipolelessness of the hexa-

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[1] See the table of dipole moments in ' Dipole Moments ', a General Discussion, *Trans. Far. Soc.*, Sept. 1934. Reprint published by Gurney & Jackson, London.

[2] Bennet, *J. Chem. Soc.*, 1934, 680.

[3] Bennet, *J. Chem. Soc.*, 1934, 1179.   [4] Hassel, *Dipole Moments*, cited p. 874.

chlorodioxan [1] it appears that here, too, the fixed configuration of the six-ring occurs and that, moreover, the Cl atoms must occur two by two in *trans-* position (Fig. 31 (XIII*)). The same symmetrical structure could be inferred for one of the three well-known tetrachlorodioxans
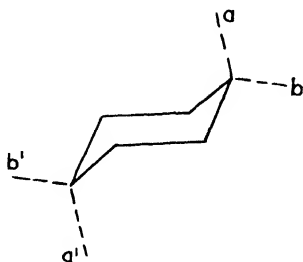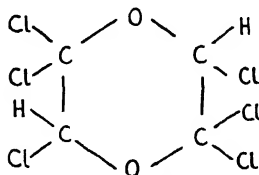
FIG. 30 (XIII*)   FIG. 31 (XIII*)

(dipoleless).[1] Furthermore, it is interesting that in the three tetrachlorodioxans the dipole moment is the greater as the melting-point lies lower; hence, according to expectation: smaller symmetry—lower melting-point, and larger dipole moment.

Mutual Interaction of Groups. We have already pointed out that accurate measurements prove that the vectorial addition of the dipole moments does not nearly yield results which are always quite in accordance with observation and that in studies on structure we may not, therefore, attach too much value to conclusions based on small differences in dipole moment.

The deviations from vectorial additivity may be traced to three causes:

(a) The valency angles can be deformed on account of the groups repelling or attracting one another.

(b) The dipoles can, through induction, increase or decrease one another's moments or change the direction of the moments.

(c) The groups can affect one another via an interjacent carbon atom or via a chain of interjacent carbon atoms.

It will generally be very difficult to pursue these influences individually. Below we shall discuss a number of cases:

(1) The mutual influence of the Cl atoms being bound on one carbon atom is illustrated by Table 9.

(2) The methylmonohalogenides have a slightly smaller moment than the ethyl- and butyl- compounds. The difference is not big (± 0.2 D), but seems to be distinctly pronounced.

TABLE 9

Substance	Found	Calculated
CH_2Cl_2	1·6	2·1
$CHCl_3$	1·2	1·9
$CH_3—CCl_3$	1·6	1·9

[1] Böeseken, Tellegen and Cohen Henriquez, *Rec. trav. Chim.*, 1935, *54*, 733.

TABLE 10

ortho-Substituents		r in D found	r in D calculated
F	F	2·58	2·5
Cl	Cl	2·24	2·7
Cl	Br	2·13	2·6
I	I	1·70	2·25
Cl	CN	4·73	4·87
Cl	NO$_2$	4·33	4·93
NO$_2$	Br	4·20	4·90
NO$_2$	CN	6·19	6·75
NO$_2$	NO$_2$	5·98	6·90

(3) The heptachloropropane may be imagined as originated by replacing one Cl atom by one H atom in the dipoleless octochloropropane. The monochloropropane may be imagined to have originated through the replacing of one H atom by one Cl atom in the dipoleless propane. Thus, if the rest of the molecule had no influence on the moments C—Cl and C—H, the heptachloropropane ought to have the same moment as the monochloropropane. This, however, is by no means the case, the moment of the latter compound being 2·0 D and of the former compound only 0·8 D. From this it is clear that the C—Cl moments interact in such a way as very distinctly to diminish each other's magnitude.

(4) The *ortho-* derivatives of benzene have a smaller moment than should follow from the vectorial additivity (see Table 10).[1]

(5) There is strong evidence to the fact that groups in the *para-* position, too, influence one another's dipole moments. This influence seems to be very strong between NO$_2$ and NO groups on the one side and the NH$_2$ group on the other, as is evident from the measured and computed moment values. The NH$_2$ group and the NO group not possessing an axial-symmetrical moment, an exact calculation is not possible, but it *is* possible to indicate a limit below which the calculated value must lie in any case (see Table 11).[1]

There are even indications of there being an interaction between NO$_2$ and Cl or Br, as is likewise evident from Table 11.

TABLE 11

para-Substituent	r found	r calculated
NO$_2$—NH$_2$	6·4	< 5·5
NO$_2$—N(CH$_3$)$_2$	6·87	< 5·5
NO—NHCH$_3$	7·38	< 5·7
NO$_2$—Cl	2·57	2·40
NO$_2$—Br	2·65	2·43

[1] See the table of dipole moments in 'Dipole Moments', a General Discussion, *Trans. Far. Soc.*, Sept. 1934. Reprint published by Gurney & Jackson, London.

(6) In a number of unsaturated compounds dipole values were found which are either abnormally low or abnormally high. A number of these cases as compared with the saturated compounds is given in Table 12.[1, 2]

TABLE 12

Subst.	r		Subst.	r
Furane	0·67		Tetrahydrofurane . . .	1·68
Thiophene	0·54		Tetrahydrothiophene . .	1·87
Selenophene	0·41		Tetrahydroselenophene .	1·79
Pyrrol	1·80		Pyrrolidine	1·57
Pyridine	2·11			
Quinoline	2·25			
iso-Quinoline	2·52			

In the compounds derived from pyron[3, 4] and the corresponding sulphur compounds, too, abnormally high moments were found (Fig. 32 (XIII *)). One has tried to account for this by assuming that there exists an equilibrium between the 'conventional' state and 'excited' states, brought about by a 'shift' of electrons (see examples in Fig. 33 (XIII *) and Fig. 34 (XIII *)).

This pretended occurrence of 'excited' conditions is called 'resonance'. The adoption of resonance is not only based on dipole measurements; a definite judgment about the fact whether it is a satisfactory hypothesis cannot be given as yet. The reader who is interested in

FIG. 32 (XIII *)

these matters may read the publications of *Hunter, Sutton, Partington, Sidgwick,* and *Zahn.*[3, 4, 5, 6, 7, 8]
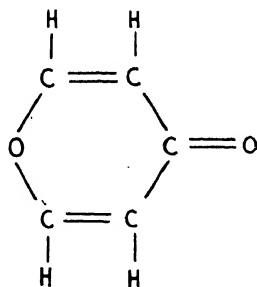
Free Rotation. Let us consider dichloroethane (Fig. 35 (XIII *)). It is assumed that the two halves of the molecule are more or less 'freely rotatable' with respect to each other. According to this assumption a dipole value should be found lying between the value for the *trans*-position ($r = 0$) and the value for the *cis*-position ($r = 2\cdot6$ D). This was found indeed.

As we do not know the forces which the Cl atoms exert upon one another, no exact calculations can be made about the moment to be expected;

[1] See the table of dipole moments in 'Dipole Moments', a General Discussion *Trans. Far. Soc.*, Sept. 1934. Reprint published by Gurney & Jackson, London.
[2] de Vries Robles, 1937 Thesis, Amsterdam.
[3] Sutton, *Dipole Moments*, cited previously, p. 801.
[4] Partington, *Dipole Moments*, cited previously, p. 823.
[5] Sutton, *Dipole Moments*, cited previously, p. 789.
[6] Zahn, *Dipole Moments*, cited previously, p. 811.
[7] Sidgwick, *J. Chem. Soc.*, 1936, 539, and 1937, 694.
[8] Hunter, *The Electronic Theory of Chemistry*, 1934. Published by Edward Arnold & Co., London.
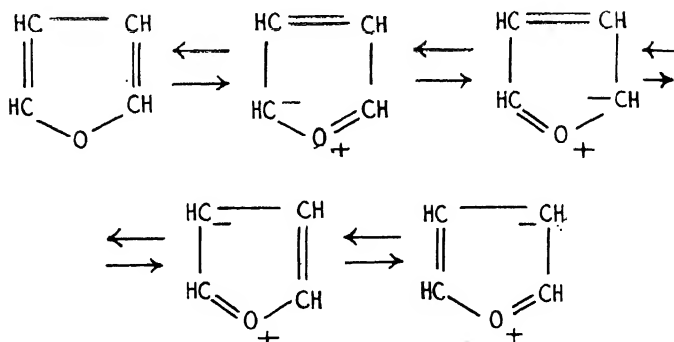
FIG. 33 (XIII *)

a priori, however, it is probable that the dipole moment must be dependent on the temperature. The lower the temperature, the more the molecule will approach a state in which it occupies a condition of equilibrium (the *trans-* position with $r = 0$ would be the most probable), and the higher the
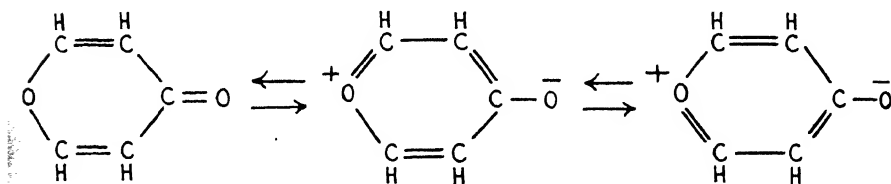

FIG. 34 (XIII *)

temperature, thus the more vehement the motion of temperature, the more a condition would have to be approached in which ' all positions are equally probable '. The dependence on temperature was found indeed. It was also found that the moment is dependent to a great extent on the solvent. This, too, is not surprising, if we realize that the forces which two molecule halves exert upon each other, are dependent as well on the medium in which the molecule finds itself. It might be expressed as follows : the force-lines running between both molecule halves must pass through the medium.

FIG. 35 (XIII *)

Mizushima, Morino, and *Higasi* [1] found for the dipole moment of 1·2 dichloroethane in hexane at − 50° 1·13 D and at 50° 1·42 D. Also in the dimethylacetal of formaldehyde : $CH_2C(OCH_3)_2$ they found a clear dependence on temperature, viz. at 55° the dipole moment of this substance measured as gas was 0·81 and at 200° 1·13 D.

The dipole moment of 1·2 dichloroethane dissolved in benzene or in toluene is about 1·75 D and almost independent of the temperature (see also work of *Meyer* and *Zahn* [2, 3, 4, 5]).
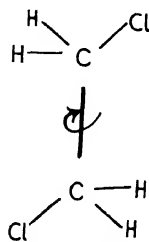
[1] Mizushima, Morino and Higasi, Sci. Papers, Inst. Phys. Chem. Research (Japan), 1934, *25*, 159.

[2] Meyer, *Z. physik. chem.* 1930, *88*, 27.   [3] Meyer, *Phys. Rev.,* 1932, *40*, 291.

[4] Zahn, *Phys. Rev.,* 1931, *38*, 52. -   [5] Zahn, *Phys. Zeit.,* 1931, *32*, 260.

If in 1·2 dichloroethane CH_2 groups are inserted between the two molecule halves, the influence which the two Cl atoms exert upon each other will be smaller the greater the number of CH_2 groups is. When three CH_2 groups are present, this influence has practically become nil. The two C—Cl dipoles then behave as if they were perfectly independent of each other, they can quite freely direct themselves, because they are separated by an adequately long 'flexible' hydrocarbon chain.

If two polar groups in a molecule are really independent of one another, that is to say, if the chain between them is long and 'flexible', the polarization though orientation must be equal to the sum of the polarization through orientation of each group apart. Thus $ClCH_2(CH_2)_nCH_2Cl$ must have a polarization through orientation twice as large as $CH_3(CH_2)_nCH_2Cl$.

FIG. 36 (XIII *)

In Fig. 36 (XIII *) the polarizations through orientation are compared for the series $CH_3(CH_2)_nCOOC_2H_5$ and $COOC_2H_5(CH_2)_nCOOC_2H_5$.[1] For $n > 3$ the polarization through orientation of the last-mentioned series of substances is really twice as
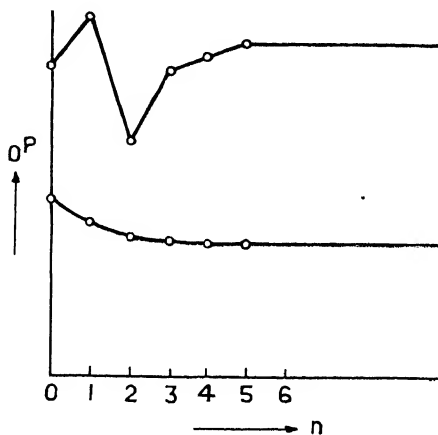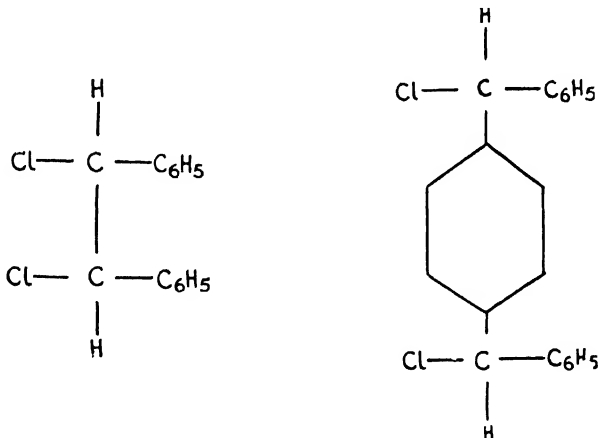
FIG. 37 (XIII *)

large as for the first-mentioned series. Note the anomalies for the first homologues of the series.

Also by interposing a benzene nucleus the mutual interaction of two dipoles is strongly diminished. An interesting example was reported by

[1] Ebert and Hojendahl, *Z. phys.-Chem.*, 1932 (B), *15*, 74.

Weissberger.[1] He found for the moment of mesostilbene-dichloride 1·27 D, and of meso-dichlorodiphenylparaxylene 2·28 D, this pointing to the fact that in the latter case the dipoles disturb one another far less than in the former case (see Fig. 37 (XIII *)).

The problem of the obstruction of free rotation (as with 1·2 dichloro-ethane) was also attacked by other physical methods, e.g. interference of Röntgen [2, 3] and electron-rays,[4, 5] Raman spectra [6, 7, 8] specific heats.[9]

Relation between Dipole Moments and other Physical and Chemical Properties. It is not the right place here to enter more fully into the connexion that was sought between the dipole moment and other physical and chemical properties. We may point to the very interesting work of *van Arkel* and *Snoek* about the influence of the dipole moment upon the boiling-point and the solubility of substances.[10, 11, 12, 13, 14, 15, 16]

[1] Weissberger, *Z. phys. Chem.*, 1930 (B), *8*, 113.

[2] Debye, *Phys. Zeit.*, 1930, 142.   [3] Ehrhardt, Thesis, Leipzig, 1931.

[4] Wierl, *Phys. Zeit.*, 1930, *31*, 366.   [5] Bergmann, *Phys. Zeit.*, 1931, *32*, 263.

[6] Kohlrausch, *Z. phys. Chem.*, 1932, *18*, 61.

[7] Mizushima, Morino, and Higasi, Sci. Papers, Inst. Phys. Chem. Research (Japan), 1934, *25*, 159.

[8] *Ibid.*

[9] Wagner, *Z. phys. Chem.*, 1931 (B), *14*, 166.

[10] van Arkel, *Rec. trav. Chim.*, 1932, *51*, 1081 ; 1933, *52*, 733 ; 1933, *52*, 1013 ; 1934, *53*, 246.

[11] van Arkel, *Physica*, 1934, *1*, 343.

[12] van Arkel and Snoek, *Rec. trav. Chim.*, 1933, *52*, 719 ; 1934, *53*, 91 ; 1934, *53*, 675.

[13] van Arkel and Snoek, *Z. phys. Chem.*, 1932, *18*, 159.

[14] van Arkel and de Groot, *Physica*, 1932, *12*, 211.

[15] Wakeman, *Rec. trav. Chim.*, 1934, *53*, 832.

[16] Stevels, 1937, Thesis, Leiden (written in English).

CHAPTER XIV *

RADIOACTIVITY [1]

SECTION 1 : DISINTEGRATION

KNOWLEDGE of the conditions governing the stability of the various atomic species has grown so enormously of recent years that only a brief summary can be given here. The scope of the subject is traced in broad outline, and only the more important manipulations are described. For fuller information, standard publications on Radioactivity and allied subjects should be consulted. A full list is given in the Guide to General Reading.

It has now been well established that most of the known atomic species may exist in the form of stable or unstable isotopes. The unstable isotopes are spoken of as being radioactive. They are known as natural or artificial radioactive bodies according as they are to be found in the earth's crust or atmosphere, or are capable of being produced by artificial means in the laboratory.

The nuclear theory of the atom [2] first proposed by the late Lord Rutherford will be familiar to most. In its original form, it postulated the existence of a small and very dense nucleus surrounded by a cloud of electrons or negative units of electricity, in number equal to the positive charge on the nucleus. These electrons were pictured as describing various orbits around the nucleus, the allowed radii of which were governed by certain provisions first advanced by Bohr.[2] This aspect of atomic physics is not of concern here. The nucleus itself was, at that time, supposed to be built up of certain elementary particles which were considered to be indivisible. These particles were protons (the nuclei of hydrogen atoms) and electrons. The protons had a mass of one on the oxygen scale (O = 16) and carried a unit positive charge $(+ e)$.[3] The electrons were the fundamental units of negative electricity, and carried a charge of $- e$. The mass of the electron has been found to be 1/1840 that of the proton, or 0·00055 unit on the mass scale (O = 16). The nucleus of any atom of atomic number, A, was assumed to be built up of N protons in association with (N—A) electrons. Small deviations from the whole number rule were explained by a loss of mass consequent upon the very close association of the particles in the nucleus.

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[1] By Dr. C. O'Ceallaigh, Physics Dept., University Coll., Cork.

[2] See, for example, Darrow, *Introduction to Contemporary Physics*, Macmillan, 1927 ; Kramers and Holst, *The Atom and the Bohr Theory of its Structure*, London, 1923.

[3] $e = 4·80 \times 10^{-10}$ e.s.u. For recent work on the evaluation of this constant, see Robinson, *Reports on Progress in Physics*, 1938, Vol. IV, The Physical Society, London; Kellström, 1935, *Nat. 136*, 682 ; Bäcklin and Flemberg, *ibid.*, 1936, *137*, 655 ; Von Friesen, *Proc. Roy. Soc.*, 1936, A *160*, 424.

Modern views assume rather a different arrangement of fundamental particles in the nucleus. This has been necessitated by the identification in 1932 by Chadwick [1] of the neutron, which is an uncharged particle of mass very slightly in excess of that of the proton, and, in 1933, of the positive electron by Anderson. [2] A readable discussion of the evidence for considering the neutrons (or protons), and positive and negative electrons to be the universal building stones, is to be found in Millikan's *Electrons, Protons, &c.* (Cambridge University Press, 1935).

Natural radioactive bodies are found to break up with the emission of three distinct types of so-called radiation, namely alpha, beta, and gamma (α, β, and γ). α particles have a mass of about four times that of the proton and carry a positive charge of $2e$. These have been proved to be the nuclei of helium atoms. A most direct proof of this fact was given by the classical experiment of Rutherford and Royds, [3] in which the evolution of helium by radon was demonstrated by the methods of spectroscopic analysis. The β particles have a much greater penetrating power than alpha particles and have been proved to be negative electrons.

An intensely penetrating radiation known as gamma radiation is also frequently emitted, the nature of which has been demonstrated to be exactly similar to that of ordinary light and X-rays, and differs from these only in its exceedingly short wave-length (ca. 0·001 Å.).

These entities may be differentiated firstly by their widely different powers of penetrating matter, and, secondly, by their behaviour in magnetic fields. The fastest α particles may be completely absorbed by a few thousandths of a centimetre of aluminium. β particles are absorbed in rather a different manner, but the intensity of the most penetrating known may be reduced by half by a few hundredths of a centimetre of aluminium. Several centimetres of this metal are required in order to halve the intensity of the most energetic γ rays. In order to give an α particle an appreciable curvature, very intense magnetic fields of the order of 40,000 oersted, [4] must be employed. β particles may be bent by fields of a few hundred oerstead, while gamma rays cannot be deflected by any magnetic field.

With the advance of physics a number of atomic particles have been used as projectiles to bombard stable elements in order to disintegrate them. Many atomic species have thus been produced, some of which have been found to be themselves stable and to be isotopes of known elements. In certain cases, however, bodies have been produced which show radioactive properties similar to those of the natural radioactive bodies. These artificial radioactive substances may disintegrate with emission of negative or positive electrons depending on their mode of for-

[1] Chadwick, *Nature*, 1932, *129*, 312 ; *Proc. Roy. Soc.* 1932, *136*, 692. See also Curie and Joliot, *L'Existence du Neutron* (Hermann, Paris, 1932), for an elementary account of the history of the discovery of the neutron ; and for a more modern account, any of the standard texts on nuclear physics (see Bibliography).

[2] Anderson, *Phys. Rev.* 1933, *43*, 491 ; see also Curie and Joliot, *L'Électron Positif*, (Hermann, Paris, 1934).

[3] Rutherford and Royds, *Phil. Mag.* 1909, *17*, 281.

[4] The electromagnetic, and practical unit of magnetic field is known as the oersted, and is of such a strength that a unit magnetic pole placed on it experiences a force of one dyne.

mation. It is frequently found,[1] especially for the lighter elements, that the stable isotopes have masses representable by a number of successive integers. Isotopes having masses greater or less than the highest or lowest stable masses, are found to be radioactive. The methods usually employed to produce such artificially active bodies involve the use of a large and expensive plant,[2] consisting essentially in an arrangement of discharge tubes and accelerating electric or magnetic fields, and are thus beyond the reach of all but specialized laboratories. By such means sources may be prepared of intensities comparable with those obtainable from the strongest natural sources. If, however, smaller quantities of artificially radioactive substances be required, recourse may be had to methods of production by neutron bombardment. A very brief description of these methods together with a convenient method of preparing a source of neutrons is given later in this chapter.

Law of Radioactive Disintegration. Radioactive bodies have been found to decay at a rate which cannot be influenced by any known means. This rate is independent of the state of chemical combination of the element, and is not affected by a change in physical state. Experiment has shown the law to be an exponential one, and it may be deduced theoretically on the assumption that the number of atoms in a given sample of a radioactive element breaking up per unit time is proportional to the number of individual atoms present in the sample at the instant chosen for observation. In other words

$$-\frac{d\mathrm{N}}{dt} = \lambda \mathrm{N} \qquad . \qquad . \qquad . \qquad (1)$$

Integration of this expression with respect to time leads to

$$\mathrm{N} = \mathrm{N}_0 e^{-\lambda t} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

where N = number of atoms present at a time t, N_0 is the number present at a time $t = 0$; λ is known as the disintegration constant of the element in question, and it expresses the number broken up per unit time.

The half-life period of a radioactive element $(\mathrm{T}_{\frac{1}{2}})$, is the time required for the number of atoms present of the body to have been reduced to half the number initially present. Substituting in (2), $\mathrm{N}/\mathrm{N}_0 = 1/2$, we find

$$\mathrm{T}_{\frac{1}{2}} = \frac{\log_e \frac{1}{2}}{\lambda} = \frac{0 \cdot 693}{\lambda} \qquad (3)$$

It will be clear from these considerations that, if after a time $\mathrm{T}_{\frac{1}{2}}$ one-half of the atoms in a given sample have been disintegrated, then after a time $2\,\mathrm{T}_{\frac{1}{2}}$, 3/4, after a time $3\,\mathrm{T}_{\frac{1}{2}}$, 7/8, and after a time $4\,\mathrm{T}_{\frac{1}{2}}$ 15/16, &c., &c., will have broken up. An infinite time is required for the complete disappearance of the body.

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[1] See Feather, *Introduction to Nuclear Physics* (Cambridge), 1936, p. 77; Rasetti, *Elements of Nuclear Physics* (Blackie), 1937, Chap. I.

[2] For a short account of such methods, see Livingston and Bethe, *Rev. Mod. Physics*, July, 1937, *Vol. 9*, No. 3, where full references to the literature may be found. See also Cockcroft, *J. Sci. Inst.*, 1939, 16, 37; *J. Appl. Phys.*, 9, 11, 677, 689.

[3] Compare monomolecular reaction, Vol. I, p. 645.

Mean Life. The mean life of an atom of such a body is

$$\int_0^\alpha \lambda t e^{-\lambda t} dt = \frac{1}{\lambda} \qquad . \qquad . \qquad . \qquad (4)$$

and is thus the reciprocal of the radioactive decay constant.

Radioactive Families. The known natural radioactive bodies may be divided into three major groups, the various members of which are formed by a chain of successive disintegrations starting from a parent body of long life. These parent bodies are Uranium, Protoactinium, and Thorium, and the series derived from them are known respectively as the Uranium, Actinium, and Thorium series. A table explanatory of their modes of production and interrelationships is given, together with the values of their half-life values and decay constants.

It will be noted that the decay constants of the parent bodies are exceedingly small; in other words, they are endowed with a very long mean life. This accounts for their relative abundance, since it is clear that this will be inversely proportional to their decay constants, or directly proportional to their mean lives. Further, it will be seen that the final product in each of these three families is a stable isotope of lead.

Radioactive Equilibrium. The concept of radioactive equilibrium is of importance. It may be illustrated by a study of the steps through which an atom of radium is finally converted into one of lead. A sample of radium is found continuously to evolve a gas radon. If pure radium be sealed up in an airtight tube, it will be found on measurement that the amount of radon present tends at first to increase. This means that the radon is being formed more rapidly than it is breaking up. The rate at which it is being formed is, to a first approximation, constant owing to the very long mean life of its parent. The rate at which it is breaking up, however, depends on the amount present, and will therefore increase as more is formed by the breakdown of the radium. A time will thus be reached when the radon is breaking up as quickly as it is being formed. No further increase in the amount of radon present in the tube can therefore take place and a condition known as radioactive equilibrium has set in. Actually, the amount of radon present at any subsequent time will be found to decrease with the extremely long period of radium ($T_{\frac{1}{2}} = 1,600$ years). This type of equilibrium between a very long-lived parent and a product of short life is spoken of as secular. It follows from equation (1) that the ratio of the amount of parent to product present when such an equilibrium has been attained will be :

$$\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1} \text{ (since } N_1\lambda_1 = N_2\lambda_2) \qquad (5)$$

The equilibrium which may exist between a body like radon which has a short life, and the products of its disintegration, is of rather a different type and is spoken of as transient.

Consider the transition

$$\text{Radium} \longrightarrow \text{RaA}$$
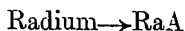
Let the number of atoms of radon present be R_0 at a time 0, and R at a time t. Similarly, let the number of RaA atoms present at a time t

equal A. Then, the rate of increase of the number of atoms of RaA will be equal to the number formed per unit time (which is the same as the number of atoms of radon broken up per unit time), less the number which disintegrate per unit time.

$$\frac{dA}{dt} = (R\lambda_R - A\lambda_A)$$

The solution of this equation yields

$$A = Pe^{-\lambda_R t} + Qe^{-\lambda_A t}$$

Since A must be zero at a time 0, $P = -Q$.
Hence :—
$$P(e^{-\lambda_R t} \quad {}_2 {}^{-\lambda_A t}$$

Furthermore, when

$$t = 0, \frac{dA}{dt} = R_0\lambda_A. \quad \text{Hence } P = \frac{R_0\lambda_R}{\lambda_A - \lambda_R}$$

so that,
$$A = \frac{}{\lambda_A - \lambda_R} \qquad e^{-\lambda_A t}) \tag{6}$$

This expression is a maximum, at a time t, which may be found by differentiating it with respect to t, and equating the result to zero.

$$t_{max.} = \frac{2 \cdot 303}{\lambda_A - \lambda_R} \log_{10} \frac{\lambda_A}{\lambda_R} \tag{7}$$

Substituting the appropriate values for λ_A and λ_R of $3 \cdot 79 \times 10^{-3}$, and $2 \cdot 097 \times 10^{-6}$, we find that the amount of RaA reaches a maximum after a time

$$\frac{2 \cdot 303}{3 \cdot 79 \times 10^{-3} - 2 \cdot 097 \times 10^{-6}} \log \frac{3 \cdot 79 \times 10^{-3}}{2 \cdot 097 \times 10^{-}} = 2,000 \text{ secs. or } 33 \cdot 4 \text{ mins.}$$

Thus $33 \cdot 4$ minutes after the sealing off of the radon in the tube, the amount of RaA has reached a maximum. From the equation (6) it will be seen that the second term in brackets $e^{-\lambda_A t}$ quickly becomes negligible in comparison with the first $e^{-\lambda_R t}$. Hence, in a case like the one under consideration, where the parent is of long life compared to the product, the amount of product subsequent to the attainment of equilibrium will decrease at a rate determined by the decay constant of the parent. If the decay constant of the product is negligible compared to that of the parent, the reverse is true, and the product decays with its own period.

The changes in constitution of the contents of a sealed tube which initially contained radon only, may be found by an extension of equation (6). It is found that the general expression [1] for the amount present at a time t, of the N-th successive product is given by

$$N_N(t) = K_1 e^{-\lambda_1 t} + K_2 e^{-\lambda_2 t} + \ldots + K_N e^{-\lambda_N t}$$

where

$$K_1 = \frac{\lambda_1\lambda_2 \ldots \ldots \lambda_{N-1}N_1(0)}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1) \ldots (\lambda_N - \lambda_1)} \tag{8}$$

$$K \quad \frac{\lambda_1\lambda_2 \ldots \ldots \lambda_{N-1}N_1(0)}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2) \quad (\lambda_N - \lambda_2)}$$

&c.

Bateman, *Proc. Camb. Phil. Soc.*, 1910, *15*, 423.

where the subscript 1 refers to the parent body and N to the (N−1)th product of its transformation. Calculations based on these considerations show that a tube which initially contained pure radon will contain, after a lapse of about two months, no radioactive matter other than RaD and its disintegration products RaE and RaF or Polonium. Thus it will be seen that such old emanation tubes form a very convenient source of supply of these bodies and particularly of polonium. An outline of the methods in common use for separating RaD, E, and F from each other will be described later.

The number of α particles emitted per second by a gram of radium has been determined [1] both by direct counting and by measurement of the rate of evolution of emanation from a known quantity of radium, and has been found to be [2]:

$$Q = 3 \cdot 70 \times 10^{10} \text{ particles, per sec. per gram.}$$

Millicurie.[2] The activity or strength of a source is commonly expressed in terms of the activity of a known quantity of radon. Amounts of radon are usually stated in millicuries. The millicurie is the thousandth part of the curie, which is the amount of radon in equilibrium with one gram of radium. The mass and volume of the curie may be calculated directly from the equation (5). It is found to be 6·5 micrograms and would occupy $0 \cdot 66 \times 10^{-3}$ ml. at N.T.P. Since this quantity of radon is in equilibrium with one gram of radium, the number of α particles emitted by it per second must be $3 \cdot 70 \times 10^{10}$ particles. It will be clear that the same number of particles will be emitted by any other body in equilibrium with a gram of radium. An alternative mode of expression is an activity of so many milligrams of radium. Clearly the activity of a mixed source may be measured in terms of its α, β, or γ ray emission. In order to discuss the interpretation of such measurements, it will be necessary first to review briefly the more important properties of these radiations.

α *Particles* are characterized by a very feeble power of penetrating matter. They may be completely absorbed by a few centimetres of air at N.T.P. For a given energy or velocity of emission the distance an α particle can travel in any medium is a fairly well defined quantity, and is spoken of as the range (R) of the particle in that medium. The energy of the particles emitted by radioactive bodies is generally stated in Electron Volts (E.V.). The electron volt is the energy which would be acquired by an electron in falling through a potential difference of one volt and is equal to $1 \cdot 591 \times 10^{-12}$ ergs.[3] A singly charged positive ion would, of course, acquire the same energy as an electron, in falling through a given difference of potential. Since the energies of the products of radioactive disintegra-

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[1] See Rutherford, Chadwick, and Ellis, *Radiations from Radioactive Bodies*, pp. 60 *et seq.*; also Ward, Wynn-Williams, and Cave, *Proc. Roy. Soc.*, 1929, A *125*, 713; *Rev. Mod. Phys.*, July 1931, No. 3; *Report of the International Radium Standards Commission*.

[2] The International Radium Standards Commission, 1931, *3*, 427, recommends that the term curie be extended to include the equilibrium quality of any decay product of radium. See *Rev. Mod. Phys.*, loc. cit., for further information.

[3] Calculated on the basis of Millikan's value for e of $4 \cdot 770 \times 10^{-10}$ E.S.U.—adopting Bäcklin and Flemberg's value $e = 4 \cdot 800 \times 10^{-10}$ E.S.U. then 1 E.V. $= 1 \cdot 601 \times 10^{-12}$ ergs.
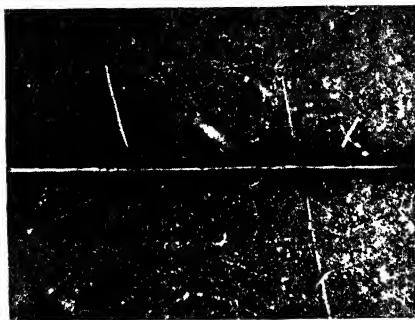
PLATE I

FIG. 1 (XIV *)

FIG. 2 (XIV *)


FIG. 3 (XIV *)

FIG. 4 (XIV *)

FIG. 5 (XIV *)

FIG. 6 (XIV *)

tions are usually of the order of many thousands of electron volts, they are usually stated in terms of Electron Kilovolts (K.E.V.), or the Electron Megavolts (M.E.V.). The energy of an α particle is chiefly dissipated in ionizing the neutral atoms of the substances through which they pass, a property which makes it possible to render visible the paths of such in the Wilson cloud chamber.

In essentials, this consists of a glass cylinder closed at the top by a glass plate. A movable piston permits of the air in the chamber being cooled by a rapid (adiabatic) expansion. If the air is saturated with water-vapour but, perfectly clean and free from dust, condensation of the vapour will occur only on the trail of ions left by passage of α or β particles through the gas. Thus the path of an ionizing particle may be seen and will be shown by filmy threads of condensed vapour which persist in the chamber for a small fraction of a second. Collisions between the various particles and atomic nuclei may be studied with this apparatus, and the occurrence of atomic disintegrations may be clearly shown. The density of a track depends upon the ionization produced by the particle which produces it. Examples of such cloud-chamber photographs are shown in Plate I, Figs. 1 (XIV *)–6 (XIV *).

Fig. 1 (XIV *). The chamber was filled with a mixture of water-vapour, helium, and air. The horizontal white line marks the position of a thin copper foil coated on its upper face with boron. The heavily ionizing particle on the left is a particle produced by the disintegration of an atom of boron by a slow neutron which came from a paraffin-surrounded source outside the chamber. The appropriate reaction is

$$_5B^{10} + _0n^1 = _3Li^7 + _2He^4$$
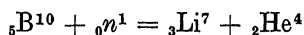
The thinner track which can be seen on both sides of the foil is probably that of a proton expelled from a water molecule in the atmosphere of the chamber through a collision with a faster neutron. The diffuse background is produced by low energy electrons ejected by γ rays from the gas molecules. (Compton and photoelectric effects.)

Fig. 2 (XIV *). An electron of medium energy (100,000 E.V.) in a magnetic field. Note the numerous deflections, in the absence of which its path would be circular.

Fig. 3 (XIV*). The magnified track of a high energy α particle showing the δ rays or electrons ejected with higher energy than the average from the molecules of the gas.

Fig. 4 (XIV *). An electron of very high energy (> 5 M.E.V.) ejected from a lead plate (P) either from a high-energy γ ray from a source outside the chamber or by cosmic radiation. Other high energy β particles are bent into circular paths by the magnetic field (600 oersted). A very slow electron is visible on the right.

Fig. 5 (XIV *). A positive electron (+) of about 800,000 E.V. energy, produced by the materialization of a 2·65 M.E.V. γ ray from a thorium source. (Pair production, negative partner not visible.)

Fig. 6 (XIV *). Another example of the same process. Two negative electrons to the left show clearly the difference in behaviour in a magnetic field. The heavily ionized and tortuous path of a slow electron serves to

illustrate the dependence on velocity of the ionization and the frequency of deflection.

It has been found experimentally that the specific ionization due to α particles rises as the velocity of the particle falls, and that it reaches a sharp maximum near the end of the range, after which it falls rapidly to zero. Such a curve is known as a Bragg curve (Fig. 7 (XIV *)). The
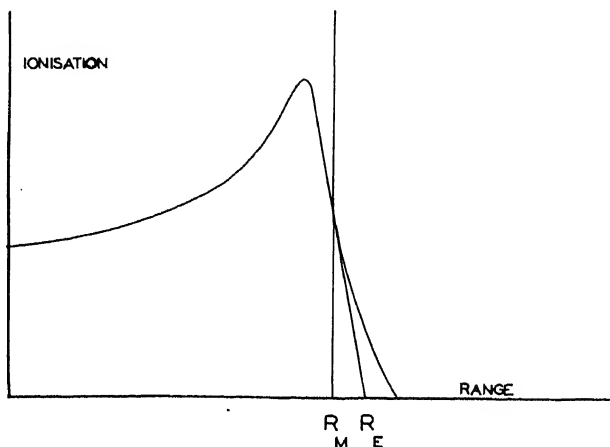

FIG. 7 (XIV *)

form of the foot of the curve is explained by the fact that the ionization is a statistical phenomenon, and that fluctuations about a mean range R_M are to be expected. R_E is known as the extrapolated range of the particle.[1] The distribution in range about the mean range is Gaussian.

An empirical range-velocity law which fits the experimental observations, at least for high velocities, has been proposed by Geiger[2] and takes the form :

$$V^3 = k(R - x) . \qquad . \qquad . \qquad . \qquad . \qquad (9)$$

where V is the velocity of a particle of range R, which has already traversed a distance x in the gas.

This simple rule fails to hold at lower velocities, partly owing to the capture and loss of electrons by the α particles from the gaseous atoms. This effect becomes of increasing importance as the velocity of the particle is reduced. Much theoretical and experimental work has been carried out of recent years on this most important question, and curves embodying the latest results are given by Livingston and Bethe.[3]

From the empirical rule (9) it may readily be deduced, assuming that the total ionization produced by an α particle is proportional to its initial energy, that the total ionization is proportional to $R^{2/3}$. For the α particles of RaC (R = 7 cm.), the total ionization is of the order of 200,000 ion pairs, rising from about 2,500 I per mm. at the beginning of the range, to

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[1] For a more exact definition of mean range and extrapolated range, see Curie, *Radioactivité* (Hermann, Paris), 1935.

[2] Geiger, *Proc. Roy. Soc.*, 1910, A *83*, 505.

[3] *Rev. Mod. Phys.*, 1937, No. 3, 9.

a maximum of ca. 6,000 I, which occurs about 5 mm. from the end of the range.

Radioactive bodies of shortest mean life are found to emit particles of greatest energy, and an empirical relationship which is in good agreement with observation has been proposed by Geiger and Nuttall : [1]

$$\log \lambda = A + B \log R \qquad (10)$$

Stopping Power. The range of an α particle of given energy in any substance divided into its range in a standard substance (usually air at 15° and 760 mm.) is called the stopping power, S, of that substance. Alternatively, if a thin sheet of any material be used to intercept an α particle, and its emergent range be found to have been reduced by a given amount, say N cm., the sheet is then spoken of as having a stopping power, for the α particle in question, of N cm.

The stopping power depends on the square root of the atomic weight of the absorber. For substances of low atomic weight, the variation of stopping power with velocity is negligible,[2] but it becomes of importance for the heavier metals such as gold and platinum. For gases heavier than air, the stopping power increases with increasing velocity. For lighter elements the reverse is generally true, but the stopping power of helium shows little variation. For complex molecules in which no association occurs, a strictly additive rule is found to apply, the molecular stopping power being the sum of the atomic stopping power of the constituent atoms.

β **Particles or Electrons.** The law of the absorption of β particles is more complex, since the paths of these particles are seldom straight lines, except for those of very high energy. The removal of electrons from a beam is due to two distinct processes, (a) energy losses due to ionization, and (b) scattering out of the beam by deflection. Furthermore, scattering may be of various types : single, plural, or multiple. A full discussion of this phenomenon may be found in any of the standard textbooks. The specific ionization due to a β particle is very much less than that of an α particle. It is greatest for slow electrons and decreases, at first rapidly, and then more slowly as the energy of the particle increases, becoming approximately constant for high energies. β particles of 10·5 E.K.V. produce about 1,000 ion pairs per (I) cm., those of 2,000 E.K.V. 96 I, and those of 3,400 E.K.V. about 70 I. The scattering of β particles increases very rapidly with falling velocity, the probability of deflection through a given angle being inversely proportional to the fourth power of the velocity. It increases with increasing atomic weight of the scattering medium. These facts are well borne out by the cloud chamber photographs (Plate I), where it will be seen that the denser tracks of the slow electrons suffer more frequent changes in their direction than those of the β particles of higher energy.

In consequence of these facts, the absorption of a beam of electrons is found to be representable by an exponential law of the type :

$$I_x = I_0 e^{-\mu x} \quad . \qquad . \qquad . \qquad . \qquad . \qquad (11)$$

[1] Geiger and Nuttall, *Phil. Mag.*, 1911, 22, 613 ; 1912, 23, 439.
[2] See, however, Livingston and Bethe, *loc. cit.*, p. 271 *et seq.*

where I_0 is the initial intensity, I_x is the intensity after traversing a distance X of the absorber, and μ is known as the linear absorption coefficient.

Other ways of expressing this absorption coefficient are frequently found :

$$\mu_M \text{ the mass absorption coefficient} \quad = \frac{\mu}{\rho}$$

$$\mu_e \text{ absorption coefficient per electron} = \frac{\mu A}{\rho NZ}$$

A being the atomic weight, N, Avogadro's, and Z, the atomic numbers.

γ-**Rays.** The law expressing the absorption of γ rays [1] by matter is also an exponential one, and is complicated by the fact that three different modes of energy loss have been proved to occur.

(1) *Photoelectric effect*, in which the energy of the γ ray or photon is completely absorbed. This phenomenon can only occur when the photon collides with an electron tightly bound to an atom. The energy of the ejected electron will be $E_c = h\nu - W$, where $h\nu$ represents the energy of the photon, h being Planck's constant, ν the frequency, and W the binding energy of the electron to the atom. This process is of importance only for γ rays of low energy and for absorbers of high atomic weight.

(2) *The Compton effect* [2] takes place, on the other hand, when a photon interacts with an electron so loosely bound as to merit the description of free.

Application of the conservation laws shows that only part of the energy of the photon can appear as kinetic energy of the ejected electron, a ' degraded ' photon being emitted in a direction different from that of the incident γ ray. This effect predominates for high energy rays and light absorbers.

(3) *Pair Production*.[3] Here the quantum interacts with the electric field of the nucleus when all its energy is expended in creating a positive and negative electron pair, and endowing them with kinetic energy. Since the energy equivalent of the mass of a positive and negative electron is about 1 M.E.V., this phenomenon can only take place for photons of energy superior to this figure. The probability of occurrence of such a reaction increases with the square of the atomic number of the absorbing substance.

In consequence of these three different modes of conversion of the energy of γ radiation, the adsorption coefficient decreases with increasing γ ray energy, but passes through a minimum, the position of which on the energy scale is lower the higher the atomic weight of the absorbing element.

Storage of Radium : Preparation of Emanation Needles. In most laboratories the radium is stored in solution in a sealed vessel, and the gases evolved are pumped off from time to time, purified and compressed into thin-walled glass capillary tubes which may serve, according to the

[1] A full discussion of the theory of the absorption of α–β–γ radiation will be found in Rutherford, Chadwick, and Ellis, *Radiations from Radioactive Bodies* (Cambridge), 1930. Curie, *Radioactivité* (Hermann, Paris), 1934. Meyer and Schweidler, *Radioactivität* (Teubner, Leipzig), 1926.

[2] A. H. Compton, *Phys. Rev.*, 1923, *21*, 715 ; 1923, *22*, 409.

[3] See I. Curie and F. Joliot, *L'Electron Positif* (Hermann et Cie, Paris), 1934.

thickness of their walls, as sources of α, β, or γ, radiation. These tubes are commonly known as radon needles, and find a wide application both in physical and medical science. The gas which is evolved consists of radon mixed with many times its volume of various impurities derived from the chemical action of the radiations on the water and greases used to lubricate the taps and ground glass joints in the apparatus. The commonest impurities are H_2, O_2, CO_2, H_2O, together with various organic gases. The work of purification is tedious, and entails a considerable loss of time, having to be carried out in two stages. Such 'wet' methods will not be described here, and details may be found by consulting the standard works of reference.[1]

Method of Dry Preparations. Recently methods of obtaining radon from dry preparations have been worked out by Hahn and Haidenhain[2] and Erbacher and Käding.[3] Full discussion of the various factors which influence the emanating power of such preparations will be found in the original papers and, also in Hahn, *Applied Radiochemistry* (Cornell Univ. Press, and Oxford), 1936. Such perfectly dry preparations have been found to retain their emanating powers over many years, and are thus very suitable as permanent sources of radon for the laboratory.

Subsequent to preparation, these sources of radon must be pumped out by means of a high vacuum pump over a period of about 4 weeks in order to remove the very slight traces of alcohol and ether which are used in the drying process. The preparation is then stored in vacuo in the metal container which is plated on the inside with chromium.

The general design of the purifying plant will be clear from Fig. 8 (XIV *), which, together with the subsequent description, is taken from Werner.[4] It is so planned that at no stage of the operations does the radon come into contact with greased taps or ground-glass

FIG. 8 (XIV *)

joints. Instead, mercury-operated float valves, 1, 2, and 3, are employed. The metal container, L, is closed by an airtight diaphragm rubber valve which can be operated from the outside.

When sufficient radon has been evolved, the whole of the glass work is thoroughly exhausted by means of the diffusion pump connected to the limb marked H.V. The lower pressure side is N.V. The quality of the vacuum may at all times be tested by the spark gap, S. With the pump running, the cooling spiral is immersed in liquid air and the diaphragm valve slowly opened. The emanation will be drawn over into the spiral, where it will condense on the inner surface, while the permanent gases are eliminated through the pump. The speed of exhaustion should not exceed
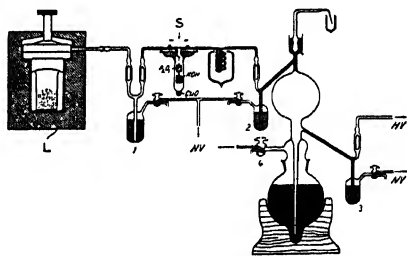
[1] Curie, *Radioactivité, loc. cit.*, pp. 169–72, &c.
[2] Hahn and Haidenhain, *Ber.*, 1926, *59*, 284.
[3] Erbacher and Käding, *Z. phys. Chem.*, 1930, *A 149*, 439.
[4] Werner, *Z. phys. Chem.*, 1933, *A 165*, 391.

0·1 litre per second in order to avoid sucking over the radon before it has had time to condense. After pumping for about 1–1¼ hours, 1 and 2 are closed by putting the two-way taps into communication with the atmosphere. The liquid air traps are then removed and the emanation, which will be mixed with small quantities of organic impurities, fills the whole volume bounded by the valves 1 and 2. These impurities are next removed through the agency of the quartz bulb, which may readily be removed for charging, being attached to the apparatus by a ground-glass joint sealed with mercury. This contains two small vessels of nickel suspended as shown, one containing KOH and the other P_2O_5. The small bulb at the bottom is filled with copper oxide activated by the oxides of palladium and lanthanum. The copper oxide preparation is heated to a dull red heat for about 15 minutes. This stage will have been completed when the discharge across the spark-gap shows the characteristic green cathode discharge.

Meanwhile the glass vessel attached to the right of 2 is evacuated by the high vacuum system, after which the pump is cut off by means of 3. 2 is then opened and the purified radon is allowed to fill the vessel. The ratio of the volume of this space to that of the space between 1 and 2 is about 20–1, so that nearly all the emanation may be compressed into the capillary T by slowly opening the tap 4. It is often of advantage to cool the capillary in liquid air while carrying out this latter operation. The tube T may then be sealed off.

It is claimed that by means of this apparatus the radon may be purified to such a degree that the volume ratio of the emanation to that of the residual impurities is 4–5 : 1. If liquid air cooling be employed, 300 mc. of radon may easily be compressed into a capillary tube of volume 0·3 mm. (10 mm. long and 0·2 mm. diam.). Space does not allow of a description of the mode of preparation of these needles, but a useful technique by which capillary tubes may be drawn having wall thicknesses down to 10μ (α ray thickness) is described in the same publication.[1]

Preparation of a Source of Neutrons. Sources of neutrons are generally prepared by exposing beryllium to the action of the α radiations from radon or polonium. The beryllium is disintegrated in accordance with the equation [2]

$$_4Be^9 + {}_2He^4 = {}_6C^{12} + {}_0n^1$$
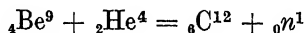
Neutrons of various velocities are produced, the energy of which will depend on the energy of the α particle which causes the disintegration. A brief sketch follows of a method of preparation of a radon-beryllium source of neutrons.

The source box may consist of a brass cylinder, S, 3 cm. in length and 0·5 cm. in diameter, turned for preference out of a solid piece of rod. The constructional details will be apparent from Fig. 9 (XIV *). The lid carries a short length of thick-walled brass tubing of small diameter such as is commonly used for connections to Bourdon gauges. The box is filled to about five-sixths of its height with finely powered beryllium. The

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[1] Werner, Z. phys. Chem., 1933, A 165, 391.

[2] Nuclear reactions such as this are usually expressed as above, the superscripts representing the isotopic weight and the subscript the atomic number of the species concerned.

lid with its tube is then carefully soldered on, care being taken to produce a vacuum-tight joint.

The working of the filling apparatus will be clear from Fig. 9 (XIV *). The box is waxed into position in the manner shown, in order to prevent the escape of the beryllium powder. S is first exhausted by means of the two-way tap and adjustable mercury reservoir. The first stages of this operation must be carried through extremely slowly in order to prevent the powder being drawn over into the glasswork where, owing to its extreme hardness, it may produce scratches which might lead to cracks at a later stage. The exhaustion may be taken to be complete when no bubbles of air are visible in the horizontal capillary limb H. The apparatus is allowed to stand for about 30 minutes, and the pumping action is then repeated. If no further bubbles are to be seen, the next stage of the operations may be commenced. This involves the transfer of the radon to the limb of the apparatus which carries the source box.

This radon is f i r s t pumped off from the source, no special precautions being taken to purify it. It is stored during the preliminary operations in a small test-tube immersed in a crucible containing mercury. It should be screened by an ample thickness of lead until the actual moment of transfer. This tube and crucible are im-
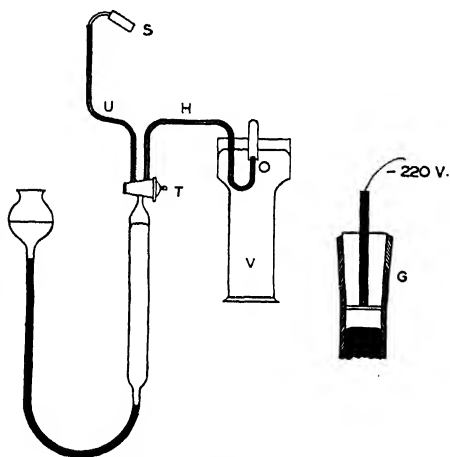
FIG. 9 (XIV *)

mersed in the mercury in the vessel V. When the mouth of the tube is well below the surface, the crucible may be removed and the tube fixed in position over the orifice, O, of the glass tube. It is then transferred to the source box by a series of manipulations which are the reverse of those required to exhaust the box. When this transfer has been effected, the tap T is closed and some cotton wool is wrapped round the horizontal portion U of the upper limb. Liquid air is then carefully poured on to the wool. After a short while, all the radon will have been condensed on the inner wall of the tube and the permanent gases may then be pumped off. The cotton wool is then removed and the radon allowed to fill the space between the tap and the box. It is then compressed into the box and the brass pressure tubing is collapsed and cut by means of a pair of pliers. Both ends of the cut so made are immediately sealed with solder. The source is finally enclosed in a suitable glass tube previously sealed at one end. The open end is then closed in the flame.

Certain effects produced by neutrons are very materially enhanced by slowing them down to thermal velocities. This may be achieved by surrounding the source by suitable thicknesses of materials rich in hydrogen

such as water or paraffin wax. It is a simple matter to cast a block of paraffin wax having a central hole in which the source is supported. The maximum concentration of neutrons at the surface of such a block is attained when the thickness of the wax is about 10 cm.

Sources by Radioactive Recoil. One of the most usual methods of preparing sources is by the method of radioactive recoil. Reference to the table of radioactive substances will show that one member of each of the three series is a gas. These gases are produced respectively by the α particle disintegration of radium, thorium X, and actinium X, and are known as radon, thoron, and actinon. When such gaseous atoms break up, it follows from the disintegration conservation laws that the expelled particle and the product nucleus will be emitted in opposite directions, and that the energy of disintegration will be shared between them. The product nucleus in the case of radon, Ra.A, may thus acquire quite a considerable velocity and is therefore spoken of as a recoil particle. Furthermore, in the majority of cases it will carry a positive charge.

For these reasons the surface of a clean wire or disc which has been placed in an atmosphere of radon will be found to have acquired a coating of radium A and the products of its decay. An exposure of a few hours will result in quite a considerable acquired activity, but the process is greatly accelerated and the resultant activity increased if the wire be maintained at a negative potential, with respect to the walls of the container, of a few hundred volts. In order to achieve the greatest efficiency of collection, the ratio of the area of the collecting surface to that of the walls of the containing vessel should be as large as possible.

In order to prepare sources of radium-active deposit, the apparatus described under the preparation of neutron sources, Fig. 9 (XIV *), may be employed. The upper limb U carries at its extremity a small ground-glass joint. The disc to be activated is screwed into the end of a thin iron rod which is waxed into the stopper G and carries a terminal at its upper end. The inner end of the rod and that of the stopper should be ground flat so that the disc fits snugly when screwed into place. This precaution is necessary in order to reduce to a minimum the deposition of Ra.A on the inner face of the disc. The glass stopper should not be greased throughout its entire length, but a gap of about 3 mm. should be kept free at the bottom end.[1]

The radon, which need only receive a preliminary purification by sparking, is transferred in the manner already described and is partially purified by means of liquid air. The mercury level is then raised to within a few millimetres of the disc, which is maintained at a negative potential with respect to it of about 220 volts. After an exposure of about an hour, the radon is pumped off and collected over mercury, great care being taken to remove all traces before removing the stopper. The disc is then unscrewed and the stopper replaced. The final treatment of the disc consists in washing it in pure alcohol to remove any radon which may be adsorbed, after which it is heated *in vacuo* to about 400° .

Active Deposits of Thorium and Actinium. The most convenient source

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[1] In order to avoid all risk of fouling the disc with grease, its diameter should be rather less than that of the glass stopper.

of thorium for laboratory purposes is radiothorium, which has a half-life period of 2 years, and may be separated from thorium minerals by a method devised by Hahn.[1] It is usually precipitated by ammonia, from a solution to which ferric chloride has been added. The mixed hydroxides are dried in air at room temperature and spread in a shallow layer on the bottom of a dish which is placed in a metal container of the type shown in Fig. 10 (XIV *).[2]

G, which is of metal, rests on a flat metal plate B. K is an ebonite stopper which fits loosely into the mouth of G. The platinum or aluminium foil to be activated is wrapped round the brass disc P, which is supported centrally by a stiff wire passing through the centre of K. This wire carries a terminal connection at its upper end, by means of which it is connected through a water resistance W, to the negative pole of a source of potential of about 200 volts. The positive pole is joined to both G and B. After an exposure of about 2 days, the activity of the wire will be approximately a maximum when the foil may be removed. The activity will be found to decay with the period of thorium B (10·6 hours) and it forms, especially if high intensities are not required, a very convenient source of α, β, or γ radiation. No danger of permanent contamination exists owing to the absence of any products of long life. The efficiency of collection will depend on various factors, one of the most important of which is the emanating power of the radiothorium. A full discussion of this will be found in Hahn.[3] The method of collect-

FIG. 10 (XIV *)

ing the active deposit of actinium is exactly the same as that which has just been described.
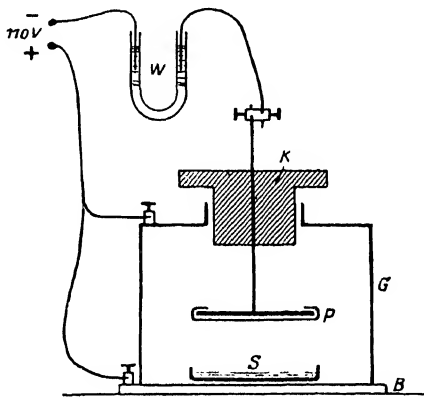
Space does not allow of a detailed description of the methods available for the separation of the various elements RaA, B, C, D, E, and F, from each other, in order to obtain radioactively pure bodies. These methods may be subdivided into :

Physical methods, such as volatilization.

Chemical methods, precipitation with carriers often isotopic with the bodies it is desired to obtain.

Electrochemical methods, controlled electrolysis, electrochemical substitution, &c.

For full details the reader is referred to the following works : Rutherford, Chadwick, and Ellis, *Radiations from Radioactive Substances* (Cambridge, 1930), 127-8 ; Meyer and Schweidler, *Radioaktivität* (Teübner, Leipzig,

[1] Hahn, *Ann. der Chem.*, 1924, **440**, 121.
[2] Figs. 9 and 11 (XIV *) are from Fajans and Wüst, *Practical Physical Chemistry* (Methuen, 1930), by permission of Professor Fajans.
[3] *Applied Radiochemistry*, Chap. IX, Cornell Univ. Press (and Oxford), 1936.

1926), Chapter VI ; Curie, *Radioactivité* (Hermann, Paris, 1935), Chapters XXII to XXVI.

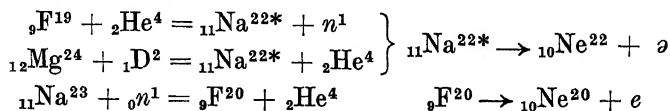The method of separation of pure sources of RaE and RaF (polonium) is important.

We have seen that, after a period of a few months has elapsed from the time of their preparation, radon needles contain only RaD with its immediate decomposition products RaE and RaF. To extract the polonium from such tubes, it is only necessary to crush them under $N/2$ HCl. When a pure silver disc is dipped into this mixed solution practically all the polonium will separate out and will be deposited in a uniform layer on the surface of the disc.

After extraction of the polonium, the RaE may be obtained by similar electrodeposition on nickel. The RaD may be recovered by electrolysis.[1] A table showing the growth of RaE and polonium from a given quantity of RaD is given by Meyer and Schweidler,[2] p. 357. From this it will be seen that the amount of RaE is a maximum after about 2 months, and that of polonium after 2 years.

It is sometimes desired to obtain a pure source of one type of radiation only, whether of α, β, or γ radiation. The production of pure γ-ray sources offers no difficulty ; indeed, the most common difficulty is the elimination of this troublesome radiation. All that is necessary is to surround the source with a thickness of lead sufficient to cut off the fastest β rays. Polonium is most frequently used as a pure α-ray source, the γ radiation from it being so weak that, for a long time, it escaped detection. RaE has similar advantages as a source of β rays of energy up to 1 M.E.V. If a beam of β rays free from γ radiation be required of energy superior to 1 M.E.V., recourse must be had to magnetic methods of separation. One such method has been described by Ho.[3] Another, involving the use of a magnetic electron lens by means of which the electrons are focused round thick lead stops, has been described by Staub[4] and Davies and O'Ceallaigh.[5]

Artificial Radioactivity. Artificially radioactive bodies are produced by the disintegration of stable nuclei by means of bombarding them with α particles ($_2He^4$), neutrons ($_0n^1$), or artificially accelerated protons ($_1H^1$) and deuterons ($_1D^2$). With these latter methods we are not here concerned; they are not within the reach of the ordinary laboratory.

These artificial bodies may disintegrate with the emission of positive (∂) or negative (e) electrons according to their mode of production. Some typical reactions will serve to illustrate this.

$$\left.\begin{array}{l} _9F^{19} + {}_2He^4 = {}_{11}Na^{22*} + n^1 \\ _{12}Mg^{24} + {}_1D^2 = {}_{11}Na^{22*} + {}_2He^4 \end{array}\right\} \quad _{11}Na^{22*} \rightarrow {}_{10}Ne^{22} + \partial$$

$$_{11}Na^{23} + {}_0n^1 = {}_9F^{20} + {}_2He^4 \qquad _9F^{20} \rightarrow {}_{10}Ne^{20} + e$$

The principal method of production of bodies which decay with the

[1] Erbacher and Philipp. *Zeit. f. Phys.*, 1928, *51*, 309.

[2] *Radioaktivität* (Teübner), 1926.

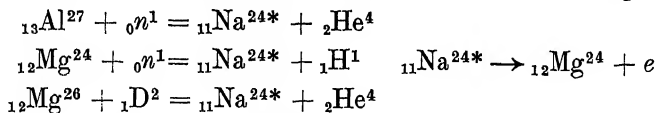[3] Ho, *Proc. Camb. Phil. Soc.*, 1934, *31*, 119.

[4] Staub, *Helv. Phys. Acta*, 1936, *9*, 306.

[5] Davies and O'Ceallaigh, *Proc. Camb. Phil. Soc.*, 1937, *33*, 540.

production of a negative electron is by bombarding various elements with neutrons. Most elements are susceptible to disintegration by this means, especially if the neutrons be slowed down to thermal velocities by means of screens of substances rich in hydrogen (so-called water effect).

Two important artificial bodies which find application in medical and physical science are Radiosodium and Radiophosphorus.

Radiosodium (Na^{24}) may be produced in any of the following reactions :

$$_{13}Al^{27} + _{0}n^1 = _{11}Na^{24*} + _{2}He^4$$

$$_{12}Mg^{24} + _{0}n^1 = _{11}Na^{24*} + _{1}H^1 \qquad _{11}Na^{24*} \rightarrow _{12}Mg^{24} + e$$

$$_{12}Mg^{26} + _{1}D^2 = _{11}Na^{24*} + _{2}He^4$$

This isotope, $_{11}Na^{24}$, has a half-life period of about 15 hours and emits β rays of energy up to 1·7 M.E.V. and, in addition, γ rays of energies as high as 3·08 M.E.V.

Radiophosphorus, $_{15}P^{32}$, has been used as an indicator in the study of metabolic processes. It may be produced by the disintegration of P^{31}, S^{32}, or Cl^{35}, by neutrons, or P^{31}, or S^{34} by diplons. It decays with the half-life period of 14·5 days, emitting β rays of energies up to 1·7 M.E.V.

A very complete list of the known radioactive elements is given by Livingston and Bethe, *Rev. Mod. Phys.*, Vol. 9, No. 3, pp. 359–61 (1937) ; see also 1st Report of the Committee on Atoms of the International Union of Chemicals, which issued in 1937 a Table of Stable Isotopes recognized to 1936, with a note on the relative abundance of particular isotopes in mixtures.

SECTION 2: MEASUREMENTS

Normally, the molecules of a gas are electrically neutral and, for this reason, gases are good electrical insulators. They can, however, be rendered conductors of electricity under the action of the radiations from radioactive bodies. The reason for this induced conductivity is to be found in the occurrence of the phenomenon of ionization. Part of the energy of the radiations is expended in removing the outer electrons from the neutral atoms. As a result of this, an atmosphere of positive and negative carriers of electricity remains, so that, if a potential difference be maintained between two metallic plates supported in the ionized gas, a current will be found to flow between them. If the source of the radiations be removed, the conductivity will be found rapidly to disappear, owing to the recombination of the ions to form neutral molecules.

The variation in the current between two electrodes well insulated from each other, and supported in a gas which is maintained in a constant state of ionization, is shown in Fig. 11 (XIV *). The current will be seen to increase up to a certain point, after which it reaches a constant value. This constant current is known as a saturation current, and is reached when the applied potential difference is sufficient to attract to the collecting electrode all the ions formed per unit time in the region between them, before they have an opportunity of recombining. At still higher voltages, the current undergoes a very sudden large increase. This coincides with the onset of cumulative ionization, or ionization by collision. This phenomenon takes place when the electric field is such that the ions are endowed with sufficient velocity to ionize on their own account. The Geiger Müller counter depends for its action on the occurrence of this phenomenon.
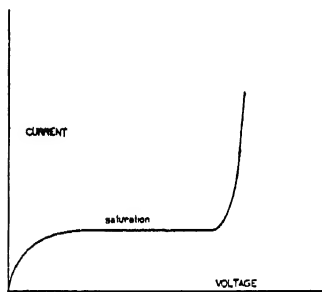
FIG. 11 (XIV *)

The ionization chamber [1] is a modification of the arrangement just described. In essentials it consists of an outer case by which a collecting electrode is supported. This inner electrode must be well insulated from the case and surrounding objects. It is maintained at a potential with respect to the case, sufficient to ensure saturation. In order to increase the ionization caused by weak radiations, the vessel may be filled with CO_2 to a pressure of 30–40 atm., or with a pure inert gas such as argon, in which the rate of ion recombination is very small even at the highest pressures. The current is usually too feeble to be measured by means of a galvanometer, so that a suitable electrometer such as a quadrant electro-

[1] See Crowther, *Ions, Electrons, and Ionising Radiations* (Arnold, 1934), Chap. II.

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meter must be employed. Details of the varieties of these instruments together with instructions for their use may be found in any standard textbook on electricity and magnetism.[1]

The principle underlying the method of measurement is briefly that, as the charged ions are collected by the insulated electrode, its potential will rise at a rate which is directly determined by its capacity ($Q = CV$). For greatest sensitivity, therefore, the capacity of the electrode system, and the associated electrometer, should be as low as possible. The collector is joined to one pair of plates of the electrometer while the other pair is earthed. The case is raised to a positive potential by means of a battery of cells of which the negative pole is connected to the earthed pair of quadrants. The ions are driven on to the collecting electrode by the field and the electrostatic repulsion causes the electrometer needle to show a deflection, the rate of increase of which is a measure of the ionization current. As this current is itself proportional to the intensity of the radiation which produces it, we are provided with a direct means of measuring these radiations and the strength of the sources from which they are derived. Instead of measuring ionization currents by the use of an electrometer, special electrometer vacuum tubes which have very high grid cathode insulations (of the order of 10^{16} ohms) may be employed. By such means, currents of the order of 10^{-14} amps.

FIG. 12 (XIV *)

have been measured, a performance which is not far short of that of the most sensitive electrometers. In order, however, to attain to this order of sensitivity, it is necessary to use balancing circuits which eliminate drifting of the zero. A full description of these methods have been given by Du Bridge,[2] and by Dowling and O'Ceallaigh.[3]

A simple instrument, which combines the functions of the ionization chamber and electrometer, finds general application in the laboratory for the measurement of the activity of radioactive sources. This instrument is the electroscope and usually takes the form depicted in Fig. 12 (XIV *). It is nothing more than a modification of the familiar gold-leaf electroscope of pioneering research.

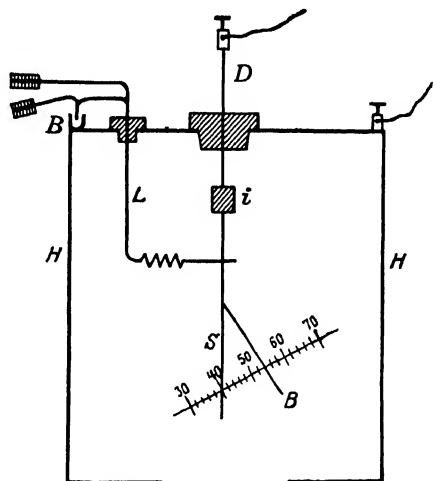The leaf system is supported by a wire D which passes through a plug

[1] See Starling, *Electricity and Magnetism* (Longmans), 1929, and Pidduck, *A Treatise on Electricity* (Cambridge), 1925.

[2] Du Bridge, *Rev. Sci. Inst.*, 1933, X, 532.

[3] Dowling and O'Ceallaigh, *Phil. Mag.*, 1935, Ser. 7, Vol. XX, 532.

of ebonite fitting a hole in the top of a metal case H. D is divided in the middle by means of a button of amber which serves to insulate it from the rest of the apparatus. The upper portion of D together with the case are earthed. L is a contrivance for charging the leaves. This is effected by rotating it until contact is made with the insulated portion of D, and then touching it with an ebonite rod charged electrically by friction. This causes the leaves to diverge owing to the repulsion of the like charges. L is then turned back and earthed by depressing the springy handle so that the small spur dips into the mercury cup soldered to the case. The leaf system is observed, through a small window, by means of a telescope carrying a graduated scale in its eyepiece.

If the behaviour of the leaves be observed in the absence of any source of ionizing radiations, it will be found that they tend to collapse exceedingly slowly. The rate of this movement depends on the quality of the insulation, and on the freedom from radioactive contamination of the walls of H and the atmosphere of the room. The quality of the instrument is judged by the magnitude of this ' natural leak ', which should be very small.

The bottom of the case may be closed with foils of varying thickness, according as it is desired to measure the ionization due to α or β rays. An electroscope designed for the measurement of radiation must be surrounded by lead and need not, therefore, be provided with a window.

If a source be supported beneath the window the leaves will be seen rapidly to collapse due to the neutralization of their charges by the capture of the ions. Their rate of movement is proportional to the ionization produced, and hence to the intensity of the source. It follows that the strength of two sources of the same material may be compared directly by observing the rate of collapse of the leaves when each is supported in turn in the same position relative to the electroscope. The two materials must be spread in layers of the same area so that the solid angle subtended by each at the instrument is the same. The decay of a source may also be followed by reading the rate of discharge at certain fixed intervals. The absorption coefficient of rays may be determined by covering the source with foils of varying thickness and observing the associated rates of discharge. The following manipulative hints may be of use.

The eyepiece is first focused on the leaf, the scale reading of which is read off relative to one or other of the edges of the leaf. A constant source of radiation is placed in position under the window. The black oxide of uranium UO_2 is convenient for the purpose. The leaf is watched throughout its travel. If it tends to. pass out of focus, the fault may be corrected by moving the telescope until the plane of motion of the leaf is parallel to that of the scale over the whole range of its travel. The time required for the leaf to pass over a given number of divisions is next plotted for different positions on the scale. If a decided drift in any given sense be apparent, the condition may be remedied by a suitable tilting of the scale. The movement of the leaf should be smooth and free from jerkiness. In measuring the activity of any source, the observed rate of displacement of the leaf (say 30 divs. per minute) must be corrected by subtracting from it the value of the natural leak (say 2 divs. per minute). The significant reading in this case is 28 divs. per minute. An alternative mode of pro-

cedure, applicable when the motion of the leaf is not uniform over all the scale, is to measure the time taken to traverse the distance between two fixed divisions, say 60 and 30. The time taken, under the natural drift, to travel between the same divisions is also observed. If these times be, respectively, 56 seconds and 15 minutes, then the activity of the source will be proportional to $30/56 - 30/15 \times 60 = 0.503$. If a comparison is being made between the strengths of two sources, the time of travel between the same divisions is measured. If, for the second source, this is found to be 130 seconds, then the ratio of the strengths of the two sources will be

$$\frac{\dfrac{30}{56} - \dfrac{30}{15 \times 60}}{\dfrac{30}{130} - \dfrac{30}{15 \times 60}} = \frac{0.503}{0.198} = 2.55$$

As the value of the natural leak is apt to vary, it should be measured each time the instrument is used.

The measurement of the activities of sources of radium and of radon needles are generally carried out with the γ-ray electroscope, which is of the same general design as that already described, except that it is surrounded by a lead screen of sufficient thickness to absorb all the β radiation. A quantity of radium sealed into a tube comes into equilibrium after about a month with those of its products which emit a penetrating γ radiation. When, therefore, equilibrium has been attained, the intensity of the γ radiation from the source will be a direct measure of the amount of radium contained in it. A standard source, containing a known quantity of radium, sealed up in the same way to prevent the escape of emanation, is placed at a distance from the electroscope which produces a convenient rate of discharge. This rate is recorded. The unknown source is then placed in precisely the same position relative to the electrometer and the rate observed. Both observations are corrected for the natural leak. This method is applicable only when both sources are approximately of the same intensity. A more accurate balance method of general applicability has been described by Rutherford and Chadwick. A short description of this method, together with much general information on the subject of standardization of sources, and the precautions necessary to ensure accuracy will be found in Rutherford, Chadwick,[1] and Ellis, pp. 562–7, and Curie,[2] pp. 325–8. Bastings[3] describes a precision instrument with automatic recording for which an accuracy of 0·1 per cent is claimed.

The Counting of Individual Particles—the Geiger-Müller Counter. The counting of the bursts of ionization due to single particles may be carried out, either by means of the Geiger-Müller wire counter (Fig. 13 (XIV *)) or by the more recently developed methods of the linear valve amplifier coupled to an ionization chamber (Fig. 14 (XIV *)). A very full account of these electrical methods of counting has been given by Wynn Williams in the *Reports on Progress on Physics*, Vol. III. (The Physical Society, 1936.)

[1] *Radioactive Substances and their Radiations* (Cambridge), 1930.
[2] *Radioactivité* (Hermann, Paris), 1935.   [3] *Jour. Sci. Inst.*, 1928, *5*, 113.
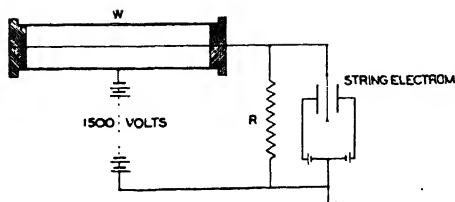
FIG. 13 (XIV *)   FIG. 14 (XIV *)
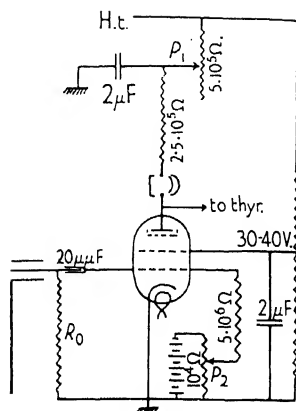
.The Geiger-Müller Wire Counter. This consists of a metal
cylinder closed at both ends by insulating ebonite plugs (Fig. 13 (XIV *)).
An inner electrode of wire is supported centrally between these plugs. This
wire usually consists of tungsten or iron, 0·1 to 0·5 mm. in diameter, and
should be free from surface irregularities. In the case of iron wires, it is
usual to oxidize it by heating to a dull red heat by means of an electric
current. The outer cylinder is provided with a window of suitable thick-
ness through which the particles to be counted may enter. The tube is
sealed with picein or other wax, and exhausted. It is then filled with air,
or a mixture of air and argon, to a pressure of about 6 cm. of mercury. It
may here be noted that the choice of material for the inner electrode, the
pressure, and the constitution of the gas mixture is largely a matter of in-
dividual choice, various workers recommending different mixtures. The
materials employed, however, should have a low photoelectric sensitivity.
A common modification of the plan just described is to enclose both elec-
trodes in a glass envelope provided with a thin glass or mica window.
Traces of alcohol vapour are often used to increase the sensitivity of the
counter. The counter case is connected to the negative pole of a battery
of cells of 1,400–1,600 volts, the positive pole of which is earthed, the inner
electrode is earthed through a resistance of about 10^9 ohms. Various
methods of making these high resistances are recommended. A simple
type consists of a small glass tube of about 5 mm. internal diameter, and
6 cm. in length. Platinum leads are sealed into the ends, and the tube is
filled with a mixture of alcohol and xylol. For other types see Brewer [1]
and Van Atta.[2]

When a constant source of radiation is brought up to the counter, the
number of particles recorded per second will depend on the applied potentials.
A typical curve representing output pulses as a function of applied voltage
is shown in Fig. 15 (XIV *). In the first rising portion, a region exists in
which the size of the output pulse will be directly proportional to the ioniza-
tion produced by the entrant particle. In the flat region, however, the
magnitude of the output pulses is independent of the ionization of the

[1] Rev. Sci. Inst., 1930, 1, 325.   [2] Ibid., 1930, 1, 687.

particle and will depend only on the counter characteristics and the leak resistance. In this region nearly every particle which enters the counter will be counted, and owing to the occurrence of cumulative ionization, the current delivered by the counter will be many times (10^6) the original ionization current which would be produced by the particle. In a good counter the extent of the horizontal portion is about 100 volts, and where it is desired to register all the particles which enter it, independent of their nature, the counter should be used in this region. By using the counter in the proportional region, α particles may be counted in the presence of a background of β and γ radiation.

In order to detect the output pulses of the counter, a string electrometer may be employed, or a valve amplifier may be coupled to the resistance and the amplified pulses made to actuate a thyratron, the anode circuit of which contains a telephone call meter. This allows of direct counting.

FIG. 15 (XIV *)

Owing to the amplification in the counter itself, the number of subsequent stages necessary is much less than for an ionization chamber, and a very convenient circuit has been described by Barasch.[1] Further details may be found in the article by Wynn Williams already referred to.

Another variety of Geiger-Müller counter is the point counter. The inner electrode consists of a sharply pointed wire supported axially in the tube, the end of which is provided with a window. The distance of the point from the window should be equal to the radius of the tube. Its properties are essentially those of the wire counter, but it may be operated at atmospheric pressure owing to the lower potentials required. This allows of the use of thinner windows.[2]
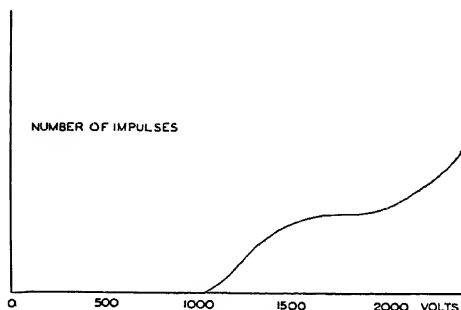
[1] Barasch, *Proc. Phys. Soc.*, 1935, *47*, 824.
[2] For further information on the functioning of Geiger-Müller counters and the associated counting equipment, see May, *Reports on Progress in Physics*, 1938, *5* ; Curran and Petržilka, *Proc. Camb. Phil. Soc.*, 1939, *35*, 309 ; Lifschutz, *Rev. Sci. Inst.*, 1939, *10*, 21.

SUGGESTIONS FOR FURTHER READING

SIMILAR 'Suggestions' are contained at the end of Volume I; and the prefatory note prefixed thereto should be read so that the limited scope of the following references may be understood. It must again be emphasized that in a rapidly growing subject like Physical Chemistry no one can keep up to date without constantly consulting such publications as the British and American *Chemical Abstracts* and *Science Abstracts* (A, Physics), and following up the references contained therein. The present 'Suggestions' have the more modest aim of enabling the general non-specialist reader to obtain further information concerning such of the topics treated in the foregoing text as he may select for further study.

CHAPTER I*. GASES AND VAPOURS

SS. 1 and 5. Vapour Pressure and Density Measurements
    See Chapter XII, S. 2, Density and S. 8, Pressure.
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    Williams. 'Low Temperature Production and Measurement', *School Science Review*, 1937, *19*, 33.
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    Egloff. *Physical Constants of Hydrocarbons*. Vol. 1. A.C.S. Monograph No. 78. Reinhold Pub. Co., 1939.
    Epschtein and Tschirkova. 'Vapour Pressure in the System $NO—NO_2$', *British Chem. Abstracts*, A1939, 371.
    Burbo and Ishkin. 'Analysis of Gas Mixtures by Determination of the Density by aid of a Gas Balance', *Zavodskaya Lab.*, 1936, *5*, 1073.
    Farkas and Melville. *Experimental Methods in Gas Reactions*. Macmillan, 1939.

This book has a well-written section on the vapour pressure of gases as well as a bibliography on the whole subject of gas reactions. Data will be found in: Annual Tables, new series, no. 27: *Tension de vapeur (1935–36)*, par Jorissen et Van Keekem; *Lois des Gaz (1935–36)*, par Keesom et Haantzes. Hermann, Paris.

S. 2. Manipulation of Gases
    See Chapter XI, S. 3, Gas Calorimetry of Volume I. See also Farkas and Melville under S. 1, both for manipulation of gases and their analysis.
    Burrell and Seibert. 'Sampling and Examination of Mine Gases and Natural Gas', *U.S. Bur. Mines Bull.*, No. 197 (1926).
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S. 3. *Gas Analysis*

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S. 4. *Liquefaction of Gases*

See references under Chapter XI, S. 4 of Volume I.

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S. 5. *Separation of Gases by Solution*

Gerver. ' Solubility of Gases in Liquids ', *Chem. Weekblad.*, 1937, *35*, 913. This deals with the effect of high pressure on solubility.

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S. 7. *Specific Heat of Gases*

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A thermodynamical treatment of distillation theory will be found in : Bronsted. *Physical Chemistry*. Heinemann, 1937.

S. 2. *Fractionation,* and *S.* 3, *Vacuum Distillation and Fractionation*

Klem—*Nature*, 1938, *142*, 616—describes the method of construction and operation of different size laboratory vacuum fractionating columns of the Podbielniak (cf. Reilly, *Distillation*, London, 1936, p. 60) type.

Wojciechowski—*Nature*, 1938, *141*, 691—applies the method of determining density of liquids by twin-pycnometer to the determination of azeotrope composition.

Elbe and Scott—*Ind. Eng. Chem.*, Anal. Ed., 1938, *10*, 284—describes a high-vacuum fractionating column which operates without gravitational reflux.

Lowe—*Gas World*, 1938, *109*, 91—applies the idea of fractional distillation being a gas-scrubbing process to the design of both plant and laboratory columns.

Lesesne and Lochte.—*Ind. Eng. Chem.*, Anal. Ed., 1938, *10*, 450—describes a new type of semi-micro laboratory fractionating apparatus. In place of the usual column packing a metal band rotating at 1,000 r.p.m. is employed.

Morey—*Ind. Eng. Chem.*, Anal. Ed., 1938, *10*, 531—gives a new method for controlling heat-input in glass fractionating columns.

Josten—*Ind. Eng. Chem.*, Anal. Ed., 1938, *10*, 165—describes a photoelectric relay to record volumes of distillate. This operates on the principle that part of a meniscus acts as an opaque plate in the column of liquid and totally reflects light striking it at an angle greater than the critical angle.

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S. 4. *Evaporative Distillation*

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Fawcett, *ibid.*, p. 43. Discusses general conditions necessary for, and technique of, molecular distillation.

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Jewell, Mead, and Phipps, *ibid.*, p. 56. Molecular distillation and vitamins.

See *American* and *British Chemical Abstracts.*

S. 5. *Distillation with Steam*

See Section 1.

Erdos and Laszlo—*Mikrochim. Acta*, 1938, *3*, 304—describes apparatus for micro-distillation with steam.

Naves—*Documentation Sci.*, 1937, *6*, 269—gives an apparatus (with the theory of its operation) for the separation of substances, e.g. volatile oils by distillation with superheated steam under reduced pressure.

S. 6. *Destructive Distillation*

Loutitt—*Mining Congress J.*, 1938, *24*, 33—describes process, &c., of destructively distilling coal in presence of superheated steam (semi-production scale).

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S. 7. *Sublimation*

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CHAPTER IV*. OTHER SEPARATION PROCESSES

S. 1. *Crystallization*
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S. 2. *Centrifugal Action*
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SS. 3 and 4.   Filtration

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CHAPTER VI*. SOME OPTICAL MEASUREMENTS

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natural crystals and fibres, applications of polarized light in industry—21 basic experi-
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' Polaroid—for Stress Determination.' Leaflet, Polaroid Co., New York, 1939.

S. 3. *Refraction*
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books, e.g. :
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mentary reading.

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1920. Although somewhat out-of-date, this book contains sound advice on
manipulation.

SS. 5, 6, and 7.   Colorimetry and Nephelometry ; Photometry and Microphotometry

In 1935 the Congress of the International Commission on Illumination (Commission
Internationale de l'Éclairage—known as C.I.E.) adopted an agreed standard of colori-
metry based upon the trichromatic method of colour specification. By means of the
colorimeter (e.g. Donaldson's) a colour measure can be made and expressed in the units
of the C.I.E. The C.I.E. system is used in various standard specifications, e.g. Brit.
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Rowland. ' Photoelectric Colorimetry ', *Ind. Eng. Chem.*, Anal. Ed., 1939, *11*, 442. *See also S. 8, below.*

S. 8. Photoelectric Effect

Rollefson and Burton. *Photochemistry and the Mechanism of Chemical Reactions*. Prentice & Hall, New York, 1939.

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CHAPTER VII*.   SPECTROSCOPY

SS. 1 *and* 2. *Spectroscopy and Spectrum Analysis*

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CHAPTER VIII*. ELECTRO-CHEMISTRY

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CHAPTER IX*.   INDICATORS

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It is intended here to list alphabetically the main topics treated, together with some special items, without making the index so detailed as to be clumsy and ineffective. No attempt is made to include the numerous authors cited. The numbers refer to the pages ; when the reference is to the ' Suggestions for Further Reading ', the number is in italics. When the page-number is preceded by ' ii.' the reference is to volume ii ; otherwise to vol. i.

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